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SORPTION OF TRICHLOROETHYLENE FROM AN AQUEOUS MATRIX BY GROUND TIRE RUBBER

By

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ABSTRACT

The purpose of this research is to examine the ability of scrap tire rubber to sorb trichloroethylene (TCE) from an aqueous matrix. The potential future extension of the research is the use of ground tire rubber as a sorbent medium for trichloroethylene and possibly other halogenated organic solvents that are present as contaminants in groundwater. The current study used batch tests to determine the equilibrium sorption capacity of the ground rubber for TCE alone. Upon completion of the batch tests, the ground rubber was used in a column test to make a preliminary assessment of its performance under the conditions of a flowing contaminant solution.

Preliminary batch tests with 310 mL of 75 ppm TCE indicated that the system approached equilibrium in less than six hours of exposure in a rotator. Isotherm sorbent capacity values ranged from 0.843 mg/g at an equilibrium concentration of 5.10 ppm to 7.16 mg/g at an equilibrium concentration of 30.3 ppm. The utilization efficiency of the ground rubber in a column test was found to be 91.5%, although no clear breakthrough of TCE was detected. Repetitive sorb/desorb tests indicate that there is no measurable reduction in performance after five iterations of the test.

The results of these tests show that the use of ground tire rubber as a medium for sorbing TCE from groundwater is promising.

CHAPTER 1.

INTRODUCTION

A great amount of time and energy has been exerted to cleanup the nation's contaminated groundwater since the implementation of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, 1980) and the Resource Conservation and Recovery Act (RCRA, 1984). These laws set the standards for contaminants at acceptable levels for drinking water. The standards of these acts have not been successfully met (Alternatives for Ground Water Cleanup, 1994).

The success of any groundwater remediation scheme depends upon the geology and nature of the aquifer, the chemical and physical characteristics of the contaminant(s) and the form of remediation used (Alternatives for Groundwater Cleanup, 1994). The long term cleanup of aquifers and sites with hydrophobic contaminants has been a problem. These non-aqueous phase liquids (NAPL) slowly dissolve into the passing groundwater flow. This requires that a remediation process be employed until essentially the source of the contaminant is exhausted. The amount of time required to achieve maximum allowed contamination levels may incur unacceptable costs, especially if an energy intensive method such as pump and treat is employed (Kershaw, 1996). Even if the maximum allowable contaminant levels were reached, that does not mean that acceptable levels of contamination will not be exceeded again when the active remediation is ceased. The cost of active remediation methods it makes more attractive the less intensive alternative methods such as passive remediation.

Passive remediation treatment methods attempt to maximize the natural biodegradation of the contaminating species or uses the natural hydraulic flow of the aquifer to push the contaminated groundwater through a permeable treatment barrier (Kershaw, 1996). The passive remediation barrier is placed in the subsurface soil below the water table. Due to the slow leaching of NAPLs into the groundwater passive treatment processes can be allowed to work at the rate of dissolution and desorption of the contaminant from the contaminated upstream soils. Treatment barriers only clean the contaminants that are carried to them in the groundwater. So as long as the contaminant is leaching from the surrounding soils, the treatment barrier must remain in place. It can be used as a containment process for a contaminant plume or as a preventative measure against future potential contamination of the groundwater supply.

Halogenated organic solvents have been improperly treated and disposed of in the past. They were and continue to be used extensively as degreasing agents in the metals processing field. Trichloroethylene (TCE) is one such solvent of significant concern. It is highly toxic to aquatic life and its maximum allowable level in drinking water is 5 ppm (Montgomery, 1996; EPA, 1994). It was recently used as part of a poisonous cocktail in a state-initiated project at Lake Davis in California to kill the lake's entire population of fish in an attempt to save the recreational fishery from illegally introduced northern pike. Upon exposure to sunlight and the atmosphere, the lifetime of TCE that is dissolved in water would only be a few weeks. However TCE usually leaches into the soil and groundwater and is prevented from being quickly degraded by normal atmospheric conditions.

Many communities receive their drinking water from groundwater aquifers that are located near an urban area. In the past, some of these areas were the site of improper disposal of halogenated organic solvent, especially TCE. TCE is present in approximately 745 of the 1,300 hazardous waste sites on the National Priorities List (NPL). Federal and state funded surveys indicate that between 9 and 34% of the sources of drinking water in the United States may be contaminated with TCE (EPA, 1994). This issue is of local concern as a community in Bucks County recently found TCE in their supply of ground water.

Granular Activated Carbon (GAC) is a widely used sorbent material for the removal of organic substances from groundwater. GAC can be used in active and passive remediation schemes and can be regenerated. Regeneration is accomplished by heating the GAC, causing the volatile organic compounds to be lost to the vapor phase. A drawback of GAC is the considerable cost of large quantities of new GAC and the costs associated with its regeneration.

NAPLs are only sparingly soluble in water. They are driven to be sorbed by the GAC because the interaction of the non-polar organics with water is not as favorable as their interactions with the non-polar GAC. It can be extrapolated that other non-polar solids could sorb TCE and other slightly hydrophobic compounds due to the same driving forces and interactions. One such hydrophobic material which the world has a dire excess of is scrap tire rubber. In 1990 alone, more than 264 million tires were sold in the U.S. while at the same time over 242 million scrap tires were generated (Miller, 1993). Recycling and reuse of scrap tires is not common and in 1990, 77.6% of the scrap tires generated were landfilled, stockpiled or illegally dumped (Kershaw, 1996).

Dumping of tires creates other problems beyond simply the space required to do so. Heaps of scrap tires pose a fire hazard. They burn at over 1500°C and extinguishing tire fires is exceedingly difficult. A fire at a tire dump near Philadelphia this past year so weakened an interstate overpass next to it that the highway had to be closed and the overpass reconstructed. Because of their toughness and resilience, they do not stay compressed and eventually work up to the surface of a landfill. Scrap tires on the surface are an eyesore. They collect water and become effective nurseries for mosquito larvae. Cutting tires into smaller chunks alleviates the above problems, but makes handling waste tires much more expensive.

Alternative uses for tires have been sought for some time. Even if that re-use may not be immediately economically self-sustaining in and of itself, the benefits of preventing whole scrap tires from being landfilled are a benefit in itself. This reuse could help offset the cost vs. benefit downside or performance shortfalls of whole or ground scrap tire rubber.

Work has been done to examine the ability of ground scrap tire rubber to adsorb and/or absorb common hydrophobic contaminants of groundwater. Previous work was with the aromatic compounds of benzene, ethyl benzene, toluene, and xylene, known collectively as BTEX (Crouthamel, 1995; Kershaw, 1996). TCE functions as an excellent solvent for grease. It should have a strong affinity for long chain hydrophobic polymers, like tire rubber, which have electronic characteristics similar to that of grease. Even if the ground tire rubber is not immediately beneficial as a financial alternative to GAC, any reuse and further degradation of this waste "resource" is a good step.

CHAPTER 2.

BACKGROUND

2.1 SORPTION AND DESORPTION

The movement of hydrophobic contaminants through subsurface geology is retarded by sorption onto soil particles and by diffusion into the soil matrix. This allows small amounts of contaminant to enter groundwater slowly. This slow, continual introduction of contaminants into the groundwater frustrates more temporary and energetic approaches to treatment. The natural desorption and diffusion processes will continue to introduce contaminant into the groundwater well after the initial plume of contaminant has passed. Organic contaminants such as those from commercial gasoline and solvents such as trichloroethylene, under study here, are only partially miscible in water. These non-aqueous phase liquids (NAPL) either accumulate above the water table or form globules with soil constituents of low polarity. These NAPL's are therefor, not readily released into the water table. This is why many "pump and treat" technologies have limited success in cleaning aquifers of hydrophobic contaminants. Passive remediation technologies have drawn interest as they can continue to intercept the contaminant as it is released from the upstream soil particles. There are many remediation technologies available, and they range from the active, high energy demand process of pump and treat to the most passive involving natural degradation and/or bioremediation of the contaminants. The ones that provide the greatest benefit with the lowest cost and effort are being examined more closely.

2.1.1 HYDROPHOBIC SPECIES IN WATER

The hydrophobicity of the NAPL's can be utilized to affect their removal. As these hydrophobic species travel through the groundwater, they will have an affinity for non-polar soil constituents and sorb onto them. Sorption is the process by which a chemical is absorbed and/or adsorbed to a solid material (Weber et al., 1991). If the affinity of the sorbate species in the aqueous matrix is high enough for a solid sorbent, then considerable amounts of the contaminant can be removed from the groundwater. The adsorption of a solute from solution to a solid at the liquid-solid interface is a complex phenomenon. In the case of trichloroethylene (TCE) and tire rubber, a fairly hydrophobic solute is leaving the polar environment of groundwater for the non-polar environment of tire rubber. Two of the predominant physiochemical forces that are driving the sorption are van der Waals forces and the "solvent hole" effect, each one contributing thermodynamically to a different degree. Van der Waals forces arise from the weak interaction of transient dipoles caused by small perturbations of electron density around a molecule. They represent four to eight kJ/mole for small molecules (Roy, et al, 1992). Another force, which can be called the hydrophobic effect, is an imperfectly understood phenomenon, but one that certainly may be a major contributor in this system. The first explanation for the origin of this force that drives the TCE to spontaneously concentrate in and on tire rubber can be thought of as a "solvent hole" effect. Water molecules interact strongly with each other via hydrogen bonding and the strong permanent dipole. The presence of a very weakly polar solvent such as TCE prevents its neighboring water molecules from this strong dipole-dipole interaction. Also, TCE is neither a hydrogen bond donor nor acceptor, because it does not have a

hydrogen atom bonded to another strongly electronegative atom, such as oxygen or nitrogen. Of the attractive forces between water molecules, hydrogen bonding accounts for twenty-one kJ/mole (Rosenberg, 1977). Due to its great relative value, hydrogen bonding can be considered as the primary driving force in this instance. For TCE to occupy space in water, (i.e. to be dissolved), it must interrupt these more favorable hydrogen bonds of interacting water molecules. It must occupy a "hole" free of hydrogen bonds and strong dipole-dipole attraction. The water and TCE could interact by weak transient dipoles, or van der Waals forces. This would cause the water molecules to then order themselves around the TCE. The ordering of these water molecules is entropically unfavorable. This unfavorable ordering would not provide other energetically favorable dipole-dipole or hydrogen bonding interactions for the water. In other words, there would be no energetic return for this process. The TCE would then be entropically driven from the aqueous matrix to allow the water molecules to produce more energetically favorable interactions with each other. The TCE could associate with the non-polar rubber surface that is mostly a polybutylene and polystyrene copolymer. Tire rubber does not have any strongly electronegative atoms to create a permanent dipole or to allow any hydrogen bonding to take place. For this reason, water does not interact strongly with the surface of the tire rubber. Hence, water does not wet the surface of rubber. The lack of interactions of water with the surface of rubber can be thought of as the water not occupying sites available for sorption. The water does not impede the TCE by interacting with or adsorbing to the hydrophobic surface. Water does not have to be displaced for TCE to sorb. This interaction would

be the first step toward absorption of TCE into the interstitial spaces of the polymeric solid.

2.1.2 ABSORPTION INTO A POLYMER

Absorption is the process in which a solute is transferred from one phase to another and penetrates the sorbent phase by at least several nanometers (Weber et al. 1991). Polymeric materials tend to absorb a greater mass of hydrophobic materials than that mass which is adsorbed onto the surface (Kershaw, 1996). The sorbate species enters the polymer matrix by diffusing into the interstitial spaces between the polymer chains. The hydrophobic sorbate then associates with the polymer chain through weak forces of attraction such as van der Waals forces. As the hydrophobic compound penetrates the surface of the polymer, the polymer chains have an ability to configure themselves to accommodate the added volume taken up by the sorbate. This micro-Brownian motion is the movement of the polymer chains within the free space of the solid polymer matrix to maximize their interaction with a hydrophobic solute (Aminabhavi and Khinnavar, 1993). This flexing changes the free spaces or channels wherein the sorbate may travel and thereby effects the ability of the sorbate to disperse further into the polymer matrix. No one part of a homogeneous polymer has any more affinity for the sorbate than any other part has, so the sorbate will disperse uniformly along the concentration gradient toward the interior of the bulk polymer. The greater the concentration gradient, the faster more sorbate enters the polymeric matrix. This results in a swelling of the polymeric matrix. This swelling phenomenon can be seen on a macro scale when large amounts of a solvent are absorbed by a polymeric material with which it has a strong interaction (Harogoppad et al.,1992; Coymn, 1986).

From the discussion presented above, the rate and amount of diffusion has an indirect dependence upon the concentration of sorbate. The increased amount of non-specific interactions of the sobate with the polymer chains causes an increased swelling of the polymer, and greater distance between the polymer chains (Harogoppad et al. 1992). This allows more sorbate to move down the concentration gradient and penetrate further into the free space between the polymer chains. These sorbate molecules increase the free space deeper within the polymer and allow additional sorbate to penetrate further down the lowering concentration gradient.

The ability of a polymer to sorb certain quantities of materials can then be seen as being largely dependent upon its ability to accommodate the finite volume of the absorbed material. Polymers that are crosslinked are much less free to create free volume in interstitial spaces. The polymer chains in such compounds are covalently linked to other chains and are not as free to move. The greater the degree of cross-linking between polymer chains, the greater the energy required to deform the polymer and the interstitial volume is lessened. Thermodynamically, this means that the concentration gradient must be increased to provide the energy for the sorption if the free motion of the polymer chain is decreased. Due to the covalent nature of the cross-linking, this has a finite point. Fillers that are added to the polymer matrix effect absorption as well. Vulcanizing uses sulfur to cross-link the polymer chains. This restricts the free motion of the chains, but does not decrease the interstitial volume much. Carbon black is a universal ingredient in the making of tires. The carbon black increases the modulus of the rubber by acting as rigid cross-links between large

numbers of polymer chains. This restricts the free motion of the chains, but also reduces the free volume available in the polymer matrix (Kershaw, 1996).

Physical and chemical characteristics of the sorbent effect the ability of it to be included in the interstitial space within the polymer matrix. Functional groups on the sorbate molecules effect the polarity of the molecule and will determine which forces energetically predominate in its association with neighboring molecules. The more similar the sorbent matrix and the sorbate are in their chemical nature, the stronger the interaction between the two, and the greater the affinity of the sorbate for the sorbent. Size and shape of the sorbate will effect its ability to enter the spaces between the polymer chains (Guo et al., 1992). A large molecule may first have to orient itself in a way that it may begin to penetrate the surface of the polymer. This organization costs entropic energy. Then the polymer chains must allow for the free space required for the larger molecule to penetrate, diffuse and weakly interact. Being large, the molecule would be sterically hindered by the finite space around it from certain conformations that would otherwise maximize these weak interactions. For these reasons, smaller molecules are more readily absorbed.

2.2 DEVELOPING ISOTHERMS FROM BATCH TESTS

Before deciding to use a particular sorbent material in a remediation plan, an investment must be made to discern if the material has an adequate affinity for the contaminant species. Batch tests are performed with the prospective sorbent on a range of contaminant concentrations. The procedures for development of sorption isotherms for TCE in an aqueous matrix to ground tire rubber are essentially the same as those developed by the EPA to determine isotherms for soils (Roy, et al., 1991). The

procedures recommended changing the mass of sorbent in the batch reactors and to follow some predetermined ratios of soil to solution ratios. If the volume of contaminant solution was held constant, and the mass varied, then unacceptable headspace volumes would result. TCE is a volatile substance and for this reason, the protocol was not strictly followed. The mass of soil, (WRF-40 granular tire rubber) and the volume of the solution were held constant and the concentration of contaminant varied. The mass of the contaminant sorbed to the ground tire rubber can be found by using Equation 1.

$$q = \frac{(Co - Ceq) \times \left(V - M/P\right)}{M} \qquad (1)$$

where:

q = sorption capacity of the solid for the solvent (mg/g)
Co = Initial concentration of the contaminant (mg/L)
Ceq = Equilibrium concentration of the contaminant (mg/L)
V = Total volume of the batch reactor (L)
M = Mass of the sorbent in the batch reactor
P = Density of the sorbent (g/L)

The sorption isotherm is derived from a plot of the sorption capacity of the solvent, (mg/g) versus the concentration of the sorbate present in the aqueous matrix at equilibrium conditions. Three mathematical models can be used to model equilibrating isotherms. These models are a simple linear isotherm, the Freundlich sorption isotherm and the Langmuir sorption isotherm (Roy, et al., 1991), (Equations 2, 3 and 4 respectively).

Linear Sorption Isotherm:

$$q = KC_{eq} \qquad (2)$$

Freundlich Sorption Isotherm:

$$q = K_f \times C_{eq}^{(1/n)} \tag{3}$$

Langmuir Sorption Isotherm:

$$q = \frac{K_l M C_{eq}}{1 + K_L C_{eq}} \tag{4}$$

where:

q = Sorption capacity of the solid for the solvent
K = Linear isotherm empirically determined coefficient (L/g)
C_{eq} = Equilibrium contaminant concentration in solution
K_f = Freundlich equilibrium isotherm empirical constant ($(L^{(1/n)}mg^{(1-1/n)})/g$)
n = Empirical constant (dimensionless)
K_L = Langmuir equilibration isotherm empirical constant (L/mg)
M = Empirical constant (mg/g)

The Freundlich and Langmuir models can be algebraically manipulated to allow for a linear relation. They then take on the form:

$$y=mx+b \tag{5}$$

They are made linear to find the unknown constants. Then the fit of each model to the isotherm data can be compared. Linear least squares will be the method used to fit the data set to the most appropriate model (Meier and Zund, 1992). As its name implies, the linear model models a linear relation with the slope of the line being equal to the constant K. The Freundlich model is not linear due to the exponent. To linearize Equation 3, the log of both sides is taken and then the form of the equation is as follows:

$$\log q = \log K_f + (1/n)\log(C_{eq}) \tag{6}$$

with the variables defined previously. The linear least squares method compares the log of the data collected from the isotherm batch tests, $\log(q)$ and $\log(C_{eq})$ and the two

constants, K_f and ($1/n$) are determined from this. K_f is taken from the y-axis intercept. It is a constant related to the affinity of the sorbate for the sorbent. The value $1/n$ is the slope which is related to how sensitive the system is to changes in concentration. The steeper the slope, the greater the effect the concentration of the sorbate has on the equilibrium point of the system. If the slope is shallow, then the mass sorbed per mass sorbate will not be effected much by changes in concentration (Stenzel, 1993; Kershaw, 1996).

Langmuir modeling of the isotherm is an alternative to the Freundlich model. It originated from the need to have a more accurate mathematical model of equilibrium sorb/desorb behavior. The Langmuir equation gives better correlation (the r^2 value) for systems that are less linear and not well described by the Freundlich equation. A plot of the Langmuir equation gives a line that rises more steeply and then flattens more abruptly than the Freundlich equation. The Langmuir equation better fits systems that deviate more from a linear relation than the Freundlich equation. The linearized Langmuir form is given by:

$$\frac{C}{x/m} = \frac{1}{K_L M} + \frac{C}{M} \qquad (7)$$

where x/m is the weight of sorbate (mg) sorbed by the weight (g) of the sorbent K_L and M are constants that can be found from the y-axis intercept and the slope of the best fit line of the data, respectively.

The model which best fits the sorb/desorb data is the one with the correlation coefficient (r^2) nearest to 1. This is found by using a simple linear regression program

either from spreadsheet software on a PC or a calculator. The values that correspond to the x and y variables are plotted and the intercept, slope and r^2 value is found. The isotherm allows one to graphically see the affinity that the sorption medium and the sorbate have for each other. The isotherm shows two characteristics of the sorbate/sorbent system that are useful: sorptive capacity changes relative to contaminant concentration and the general affinity of the sobent for the sorbate.

2.3 BED COLUMN TESTS & UTILIZATION PACKED EFFICIENCY

Any batch test is meant to examine the characteristics of a system at equilibrium. However, when used for remediation in field conditions, the sorbent does not sorb contaminant under equilibrium conditions. Packed bed column tests are the next step to determine the utility of a material as a sorbent for contaminants in ground water. Packed bed column tests help to determine the utilization efficiency of a sorbent mass under a certain flow rate or retention time and influent concentration of contaminant (Crittenden et al., 1991). In general, these tests consist of a solid sorbent media which is either wholly porous or, more commonly, shredded, ground or of a fairly fine particle size. This maximizes the surface and speeds the sorption process. The media is packed into a column that is made from an unreactive substance, usually glass. A solution made up of a matrix (in this case, distilled water) and a contaminant species of a determined concentration is run through the media and aliquots of the treated effluent are sampled downstream of the packed bed at intervals throughout the test. The sample aliquots are then analyzed to determine at what volume of effluent the contaminant species achieved breakthrough of the sorbent packed bed. Breakthrough is

defined as the aliquot where the contaminant concentration exceeds the concentration allowed in groundwater or in discharge effluent; whichever is pertinent. Column tests give some idea about remediation design requirements and therefor, are more indicative of end use sorbent performance of the medium.

The sorbent in a column test will operate under kinetic sorption conditions (Kershaw, 1996). The more readily a sorbent medium approaches its equilibrium sorption of contaminant, the more efficient it is. The utilization efficiency is the ratio of the mass of contaminant sorbed in a column test over the mass of contaminant sorbed under equilibrium conditions with the inlet concentration equal to the batch test initial concentration.

$$UtilizationEfficiency = \frac{(mg/g)Sorbed_{Column}}{(mg/g)Sorbed_{Batch}} \times 100 \quad (8)$$

The calculation for the sorbent capacity of the packed bed media is done over a period of time so that the volume of the contaminant solution and then the mass of the contaminant can be found. The steady rate and concentration of the contaminant in the influent are assumed to simulate field conditions encountered in remediation (Crittenden, 1991). Using the flow rate and the time that the test is run, the amount of contaminant passing through the column is then found from Equation 9.

$$q_{col} = \frac{\left[\left(C_{\inf} - C_{eff}\right) \times V_L\right]}{m} \quad (9)$$

where;

q_{col} = the amount of contaminant sorbed per unit mass of the sorbent (mg/g)
C_{inf} = average influent concentration (ppm)
C_{eff} = average effluent concentration of treated solution (ppm)
V_L = volume of contaminated solution treated (L)
m = mass of sorbent in the packed bed (g)

The amount of time the contaminant solution is in contact with the sorbent in the packed bed effects the utilization efficiency. The more time that the solution spends flowing through the packed bed, the more contaminant is sorbed and the closer the system gets to equilibrium. Conversely, the less time the solution takes to flow through the sorbent bed, the less contaminant will be sorbed and the lower the utilization efficiency. To compare test data, flow rates and packed bed dimensions must be reported.

Two useful values for estimating flow times and values in column tests are the empty bed contact time (EBCT) and a contact time estimated by the void volume of the sorbent media (Kershaw, 1996). The EBCT is based on the length of time that a solute particle will take to travel the length of the packed bed if it were not there. The EBCT is calculated by dividing the length of the packed column of sorption media by the flow velocity. The flow velocity is found from flow rate (volume/time) being divided by the cross sectional area of the column. The contact time based on void volume is determined by dividing the volume of the sorbent bed media by the flow rate. The void volume of the media is the space within the column that the media occupies. Once the density of the sorption media is known, the volume that a known mass of it occupies can be found.

Tracing the increase in contaminant concentration with the eluted volume around the breakthrough region gives information about the performance of the sorbent in the column. This gives the shape and abruptness of the breakthrough curve. The more sharply the curve rises from the pre-breakthrough levels, the more efficiently and

quickly the sorbent is working. If the sorbent media has a high affinity for the contaminant and approaches equilibrium conditions quickly, the breakthrough curve will be very abrupt. However, the shape of the breakthrough curve can be manipulated by slowing the flow rate to allow more contact time. The system then more closely approaches equilibrium conditions and the utilization efficiency goes up. Also, a sorbent media that absorbs much of the contaminant will require more time than one that adsorbs the contaminant onto its surface. The contaminant will have to first be adsorbed and then move down the concentration gradient into the sorbent particle. Characteristics of the sorption isotherm can effect the breakthrough as well. Consider a curve that is best modeled by the Freundlich isotherm. The lower the slope of this isotherm, the less it the sorbent will be effected by changes in the contaminant concentration. The breakthrough curve should then be sharp. The sorbent media would take-up sorbate to a certain level, dependent upon the column inlet concentration. The concentration would be roughly uniform throughout the column, and then unsorbed, excess contaminant would elute. The linearized Freundlich variable of $1/n$ should be less than 1. A value of $1/n$ greater than 1 indicates that the sorbent is too sensitive to contaminant concentration (Stenzel, 1993).

2.4 TIRE RUBBER COMPOSITON

Polymeric material in general, and specifically tire rubber have demonstrated an ability to sorb organic species (Crouthamel, 1995; Kershaw, 1996). This bulk physical property is the result of the polymerization of hydrophobic monomers. The bulk material has similar non-polar, hydrophobic properties and so is the preferred environment for hydrophobic species in an aqueous matrix.

Tires are composed of tire rubber and a supporting fiber/wire structure. When ground tire rubber is prepared from scrap tires, the polyester cord and steel wire are removed, leaving only the polymeric material and any other filler that are part of the rubber "recipe". The basic components of tire rubber can be grouped together into categories with a rough percent composition. The basic categories are as follows: elastomers, such as natural and artificial polymers, processing aids, aging resistors, (antioxidants), and softeners, such as extender oils (Park, et al, 1993). Table 1 below gives the weight percent breakdown of some specific components of tire rubber. The data in the table below shows that non-polar, carbonaceous material constitutes the bulk of the tire rubber's weight. From this, the material derives the ability to sorb hydrophobic species from an aqueous matrix.

Table 1. Common tire rubber composition

Component	Weight Percent
Butadiene	46.5
Styrene	15.5
Carbon Black	31.0
Extender Oil	1.9
Zinc Oxide	1.9
Sulfur	1.1
Accelerator	0.7

Adapted from Kershaw, 1996

The potential of tire rubber as a sorbent has not been thoroughly examined or used in remediation. A pilot test is being conducted at the University of Wisconsin, Madison to explore the utility of tire chips as an organic chemical sorbent immediately above the sanitary landfill composite liner system. There is some increasing interest in using scrap tire rubber as an environmental barrier and organic liquid sorbent. The potential desorption of hazardous species possibly contained within the scrap tire rubber

does not pose a threat to groundwater systems. Park, et al (1993) performed the EPA Toxicity Characteristics Leaching Procedure (TCLP) on a variety of scrap tire rubber that was processed in several different ways. TCLP tests use an acidified aqueous solution to speed the release of potential leachates within a solid sample matrix. The results indicate that there is a minimal threat of toxic compound leaching from ground tire rubber.

2.5 TRICHLOROETHYLENE: ORIGINS AND PROPERTIES

Trichloroethylene (TCE) has been used most extensively as a solvent and specifically a degreaser. In the past, it has been improperly disposed of by being dumped into waste lagoons. The TCE that did not evaporate found its way into the ground beneath the site and from there into the groundwater. TCE has been identified at approximately 745 of the 1,300 hazardous waste sites on the National Priorities List (EPA, 1994). Surveys conducted by federal and state agencies indicate that from 9 to 34% of the sources of water in the United States may be contaminated with TCE. TCE can be released into the atmosphere as it evaporates from coatings, glues, adhesives and other solvent-based products. The EPA has established a drinking water standard of 5 parts per billion (ppb). Combustion by mixing with fuel is the recommended method of disposal. This combustion must be complete because partial oxidation results in the production of $COCl_2$ which is highly toxic phosgene gas. There has recently been more effort put into the recovery and recycling of TCE (EPA, 1994). Table 2 below gives some properties of interest for TCE.

Table 2. Properties of trichloroethylene (Montgomery, 1996)

Property	Value
Boiling Point	87.2°C
Density	1.461 g/cm^3
Solubility in Water	1,400 mg/L at 23-24°C
Vapor Pressure	69 mm Hg at 25°C
Toxicity (LD_{50}) mice	2,402 mg/kg

CHAPTER 3.

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 GROUND RUBBER

The ground rubber used in the tests was scrap tire rubber, ground by and obtained from Baker Rubber Inc., Chambersburg, PA. It was used in the column and batch tests as received with no additional cleaning, sifting, separating or processing. The ground rubber was made from a random supply of whole passenger and/or truck tires and the like. Any other internal structures or components that were not tire rubber, such as steel or polyester chords were removed before processing. The fabric content of the final product of ground tire rubber was around 0.05% by weight. There are a variety of grain sizes of ground tire rubber available. The research presented herein which used the ground form of tire rubber used the finer size WRF-40. The mean specific gravity of the ground rubber was determined to be 1.20 g/ml (Kershaw, 1996).

Ground tire rubber was impractical to use in some of the tests, so whole chunk tire rubber was used. It was taken from blown-out tire remains found along a local interstate. The section of the tire from which rubber used in the test was taken was the outer part nearest to the tread, or was the tread itself. This minimized the possibility of having fabric or steel cable in the rubber sample.

3.1.2 TRICHOLOETHYLENE

The trichloroethylene reagent used was spectraphotometric grade, 99.5% pure trichloroethylene (TCE) (Lot # 02635AQ) purchased on 05/01/97 from Sigma-Aldrich.

To facilitate usage, 500 ml were transferred to a 500 ml bottle that formerly held a similar grade of TCE. The bottle was made of brown glass, as TCE is sensitive to light and kept in a refrigerator at 7° C to aid in preventing loss to volatilization. Purge and Trap grade methanol, suitable for GC-MS work, was used to prepare the 10,000 ppm stock solution and as a co-solvent to allow the TCE to be easily dissolved in water. It was purchased from Sigma-Aldrich as well. The acetone used for rinsing of equipment and glass wear was ACS grade Acetone purchased from Sigma-Aldrich. The deionized water was generated in proprietary stills made for that expressed purpose.

3.1.3 SYRINGES

All of the syringes used for sample injection, dilution and preparation were purchased from Hamilton Co. of Reno, Nevada. Table 3 below lists the sizes of the syringes and their primary uses.

Table 3. Syringes used in the research

Model	Capacity	Graduations	Uses
Gastight #1750	500 µL	10 µL	Dilutions of Calibration Standard and preparation of 50 mL,10,000ppm TCE stock
Gastight #1725	250µL	5µL	Dilutions of Calibration Standards and preparation of 25 mL, 10,000ppm TCE stock
Gastight #1710	100µL	1µL	Dilutions of Calibration Standards
Gastight #1701	10µL	0.2µL	Injection of headspace gas samples into GC-MS
Kloehn	5 mL	0.1 mL	Taking aliquots of TCE solution from the inlet port of the packed bed column test

3.1.4 BATCH TEST APPARATUS

All batch tests were carried out in ~315 mL glass bottles with ground glass

stoppers. They are intended for use in biological oxygen demand tests, (BOD). Due to the volatility of the TCE, there had to be as little head space (air bubble) in the bottle as possible. The BOD bottle and stopper's design is made to aid in exclusion of air bubbles from the bottle. The stopper has a pointed end and steeply sloping sides. As the user fills the bottle up to and above the ground glass neck, the insertion of the stopper excludes most air bubbles. TCE is fairly hydrophobic and has a weak dipole moment. The polar glass walls of the BOD containers then provide an inert surface. The thickness of the bottles gave them the strength to survive the physically demanding tests in the rotator for days on end.

Batch test sample aliquots of 30mL were kept in deactivated clear glass VOA (volatile organic analysis) sample vials of around 40mL volume. The vials actually held 43 ml, as was determined by filling them with water and finding the water's weight by difference. Then the volume of the VOA vial was found thorough water's density of 1 g/ml. The vials were obtained from National Scientific Company of Lawrenceville, GA. The VOA vials were sealed with screw caps having an exposed septum design. New Teflon-lined, silicon rubber septa were bought from National Scientific. The VOA vials were integral in headspace analysis, as the equilibrium concentration of the vapor phase solute of interest needs to be constant throughout repeated sampling and uniform among samples and standards. It also must form a gas tight seal to prevent, as best as possible, any loss of analyte vapor from the environment of the vial.

3.1.5 COLUMN TEST APPARATUS

One of the primary considerations in selecting, assembling and running the column test is limiting the TCE solution's exposure to air at any point. The system of

the column must be for all intents and purposes, a system closed to the atmosphere, with only the effluent sampling port being open. Two types of air exposure are possible in this system, dead air and atmospheric air. Dead air exists as bubbles or any headspace. The TCE in solution would go to vapor to come to equilibrium with the air. To minimize this, a 4 L flexible Teflon air-sampling bag was used as the influent reservoir. The influent could sit with almost no headspace and this would not increase as the TCE solution is drawn out. Additionally, the TCE would come to equilibrium with the air remaining in the bag and then stop leaving solution. This would help to insure a steady concentration of TCE throughout the test. Exposure to atmospheric air was essentially eliminated within the system by just having all connections sealed.

The TCE solution was moved into the head of the column at a steady flow rate by a piston pump by Milton Roy Company of Florida. Being as there was no exposure to the atmosphere, the pump simply replaced what flowed out of the column by gravity. The pump regulated the flow because what solution flowed out had to be replaced by solution fed into the column head. The pump operated by a piston acting on a diaphragm. Two stainless steel ball valves seated in Teflon at either end of the chamber regulated the direction of the flow of the solution. Both the piston's percent displacement and stroke rate were variable. The distance the piston moved with each stroke and the number of strokes per minuet could be regulated by dials on the back of the pump.

The glass column was custom manufactured by Glass Blowers of Turnersville, New Jersey. The threaded inlet and effluent ports of the column were made of Teflon, as was the tubing used to convey the solution from the sample bag to the column. The

only parts of the column test apparatus, which were not either Teflon, glass or stainless steel, were the Viton O-rings used as gaskets where the Teflon inlet and effluent ports were screwed into the column.

Sampling of the effluent from the column was done directly into ~5mL deactivated brown glass vials. The actual, average volume was found to be 5.15mL with the same technique as was used with the 40mL vials. Like the 40mL vials, the 5mL vials had open top, screw caps. They were sealed with Teflon lined silicon rubber septa, which allowed for the use of syringe sampling for the analysis of the headspace gasses. Sampling was done by pushing a luer lock needle attached to the end of the column through the top of the vial. The cap was loosened to allow atmospheric air to escape and as little TCE to be lost to the atmosphere as possible. The vials were filled to overflowing to reduce the headspace gasses as much as possible. However, the filling of the vial took about one minuet. The sample solution was exposed to air all this time, and so losses in TCE concentration were inevitable.

Two balances of differing precision were used, each one depending upon the requirement at the time. The balance that was used to weigh the WRF-40 and chunk rubber and for finding the average volume of the BOD bottles was an open-top, digital balance made by Denver Instrument Company. The display indicated a precision down to 1/100 grams. Informal experiments and experience with this instrument indicate it's precision to be very close to +/-0.01g. When more accurate and precise values were needed, materials were weighed on a Mettler H10TW analytical balance, with a capacity to weigh down to 0.1 mg or 0.0001g. This instrument was used primarily for

finding the volumes of the 43 and 5.2 mL VOA vials and the weight, and correspondingly, the ppm concentration of TCE in the stock solution.

3.1.6 ANALYSIS INSTRUMENTATION

All of the data collected in this segment of the research was from a Gas Chromatograph Mass Spectrometer, (GC-MS). The GC is a Hewlett-Packard (HP) 5890 Series 2 Plus. The capillary column was an HP 5 MS with dimensions of 30 m long, 0.25 mm internal diameter and a film thickness of 0.25 mm. The Mass Selective Detector, or Mass Spec. (MS) is an HP 5972 MSD coupled to the GC by an interface kept under vacuum by an Edwards #3 vacuum pump. The analysis method entailed setting parameters for both the GC for separation of the sample and the MS for quantitative detection of the TCE. All parameters were set and enacted using the HP PC that controlled the GC-MS and processed and store data from the instruments. A 5μL sample of headspace gas was manually injected into the injection port of the GC using a Hamilton Gastight #1701, 10 μL syringe. The mobile phase gas was 99.999% Helium.

3.2 METHODS

3.2.1 GLASSWEAR CLEANING

Due to the volatile nature of TCE, it does not remain for long periods of time on utensils and so does not give rise to lingering cross-contamination. However, to maintain the integrity of the test data, the systems should be free of any other contaminant, solvent, or particulate matter. Therefore, cleaning of glassware must be thorough and uniform.

Before the initial use, all glassware (BOD bottles, pipettes, volumetric flasks, and column) was washed in an Alconox detergent solution, and then rinsed three times with warm tap water. Most of the tap water was allowed to drip out. Then the glassware was rinsed three times with distilled water and then again the water was allowed to drip out. One thorough rinse with acetone finished the washing process, and after the excess acetone was poured off to waste, the remaining solvent was allowed to drip out to dryness. The glassware was then allowed to sit under a hood, exposed to the atmosphere to allow all of the remaining solvent vapors to evaporate and leave a clean and dry piece of equipment.

Subsequent washings of glassware that was not directly exposed to any rubber sorbent material, either chunk or ground WRF-40, was rinsed only with distilled water, acetone, and allowed to dry.

3.2.2 CHEMICAL DILLUTION

All dilutions of TCE solution to the desired concentration followed a two step process. The first step was the preparation of a stock solution of TCE with a known concentration which shall be referred to as the working stock. This is prepared according to EPA methods (EPA, 1991). The only exception was that, for the practical purpose of needing large amounts of the stock solution, a 25 or 50mL stock solution was prepared. It was decided that a 10,000 ppm stock solution would be the most convenient for preparing the levels of TCE solutions for both calibration standards and experiments. This stock was then used directly without any further dilutions.
First, the amount of spetrophotometric grade TCE required for the 10,000 ppm stock was calculated. An example is shown here.

$$\text{Concentration of standard} = \frac{(\text{volume of trichloroethylene})(\text{density})(\text{purity})}{\text{Volume of methanol}} \quad (10)$$

A 1 ppm solution contains 1mg of solute per liter of solvent or 1μl per mL of solvent.

So, for a 10,000 ppm solution, an example calculation is given below.

10,000 ppm TCE in MeOH = (10,000μg/1mL MeOH)(25 mL) = 25,000 μg

Or, upon conversion, 250 mg of pure trichloroethylene is needed.

So:

(250 mg pure TCE)(1μL/1.463mg) (100/99.5)= 171.7 μL of the TCE reagent/25 mL MeOH.

A more accurate value for the ppm TCE stock prepared was found by using the weight of TCE added to the volumetric flask, partially filled with methanol.

$$\text{Stock TCE} = \frac{(\text{mass of TCE added})(\text{purity})}{(\text{volume})} = \frac{(252.8\text{ mg})(.995)}{.025\text{L}} = 10{,}061\text{ ppm TCE} \quad (11)$$

The amount of the TCE stock solution needed for dilution and further use could then be calculated from this value. The additional step of finding the true value of TCE added was needed because the graduations on the syringes were not appropriate for such an accurate measure. Also, some of the TCE would volatilize into the headspace of the flask. The system was allowed to come to equilibrium before the final weighing. As a further example, the following calculation shows the amount of the above stock needed for the preparation of a 30mL calibration standard of 75 ppm TCE concentration.

$$\text{Volume of stocked to inject} = \frac{(\text{Desired concentration of standard})(\text{volume of standard})}{(\text{Concentration of stock})} \quad (12)$$

$$\text{mL of stock} = \frac{(75\ \text{ppm})(35\ \text{mL})}{(10{,}061\ \text{ppm})}$$

The volume of standard to inject is then 261μL.

3.2.3 METHOD OF ANALYSIS AND CALIBRATION

The Gas Chromatograph-Mass Spectrometer system can be completely controlled by a personal computer (PC) dedicated to running the instrument. The parameters of analysis can be set on the PC, stored by the PC and then recalled and run. The control of the analysis breaks down into the control of the separation of the sample, performed by the GC, and the detection and further analysis of the sample, performed by the MS. Identical conditions are required to obtain results that are quantitatively significant, and the GC-MS system provides for that.

The method used for analysis was to sample the headspace gasses over the sample with a gas tight syringe. No established EPA or ASTM method could be directly applied to the parameters of this analysis. All of these methods used either direct injection of the liquid sample matrix (EPA Method 8010B, 8120A) or a purge and trap method (EPA Method 502.1). No purge and trap equipment was available. Otherwise, this would have been a desirable method. Direct injection of a sample in an aqueous matrix could, and would, over continued practice, damage the stationary phase of the column. Although direct aqueous injection has been used in previous, related research (ASTM D 2908-91), the GC-FID instrument was used exclusively by the researcher. A compatible column was installed. An FID is not applicable to detecting

dilute levels of compounds that are highly substituted with halogens. For maximum sensitivity with an FID detector, the compound should be flammable. With three chlorine atoms and one hydrogen, TCE is not considered flammable. Extracting the TCE into an organic solvent would be possible (EPA Method 3510B), but this presents other challenges. The separatory process would have losses of sample due to volatilization. The process of liquid-liquid extraction is also work intensive and time consuming. Given these limitations and challenges, headspace analysis was deemed appropriate.

Sampling procedures evolved throughout the course of the analyses. Originally, the tests that contained ground rubber were filtered or strained in glass filtration funnels with glass wool used as the filtering medium. This allowed far too much TCE to be lost from the sample. Eventually, the method was found where a 30 mL Class "A" volumetric pipette was used to take-up the sample directly from the BOD bottle. A delivery of 30 mL of sample into the VOA vial allowed for around 13 mL of headspace from which to sample. Upon establishment of gas phase/liquid phase equilibrium, repeated sampling of 5 μL aliquots of gas should not deplete the amount of TCE present in the bulk aqueous sample to any detectable extent.

The packed bed column test used ~5 ml VOA vials to collect aliquots from both the inlet sampling port and from the stopcock at the bottom of the column. A much closer approximation of the small VOA vial volume was found by the weight of water required to fill the vial completely and with no headspace. This average value was found to be close to 5.1 mL. The VOA vials used for sample aliquots were filled completely with no headspace and then 1 mL was taken from them with a syringe to

allow for headspace sampling. The standards were prepared by injecting 4.1 mL of DI water into the vials and then adding the appropriate volume of stock solution.

Every effort was made to allow the ground rubber to settle before sampling from the BOD bottle, but some remained suspended. Any agitation, such as current induced by the uncapping of the BOD bottle, introduction of the pipette and the uptake of sample caused additional ground rubber to be stirred-up and taken into the pipette. The amount of rubber was very small as only a very few (10-12) tiny rubber grains could be seen in the solution in the vial. Equilibration was found to occur in less than 24 hours, so any small rubber particles would already be at equilibrium with the TCE in the sample. Also, their mass was so small that any additional sorption that took place would not be significant.

A recent application note published by Hewlett Packard (Doherty, 1993) discusses the use of GC with an MSD for the quantitative analysis of pesticides. These compounds are more commonly detected using an Electron Capture Detector (ECD), due to the presence of the electronegative chlorine. TCE lends itself well to headspace analysis because of its volatility. Also, repeated direct injection of aqueous samples can harm the stationary phase of the GC column so gas phase headspace sampling is preferred. The calibration standards were allowed to sit for one hour in the dark, (TCE is sensitive to light), to allow the TCE in solution to come to equilibrium with the gas phase. A 10 μL Hamilton Gastight syringe was used to sample 5 μL of headspace gas. The piston was pumped at least 3 times in the sample headspace, starting from zero volume, to dilute the atmospheric gasses present in the needle. Direct, manual injection was used to introduce the sample. The needle was allowed to stay in the injection port

for 0.08 minuets with every injection to allow for sample that was not pushed out of the needle end to disperse into the carrier gas stream. The MSD was set to detect only the base peak of 95 atomic mass units (amu), because this mass is characteristic of the ion fragmentation of TCE. Because of this exceedingly selective detection mode, good separation of the sample constituents was not necessary. The complete elution time of the TCE peak was from 1.8 minuets to 2.7 minuets giving a very broad peak. Retention times were 2.1 minuets, and ranged before and after this by less than 6 seconds. The entire analysis was set to end in 3.7 minuets, as all of the TCE had eluted well before then. The chromatogram of the Total Ion Chromatogram (TIC) with the MSD operating in Single Ion Monitoring mode (SIM) was collected by the PC using Hewlett Packard software. The area under the elution peak corresponding to TCE (the only peak present) was automatically integrated. This area is directly proportional to the amount of the analyte being detected, which is in turn directly proportional to the amount of TCE in the injected sample. The amount of TCE in the headspace of the calibration standard VOA vial is proportional to the concentration in the aqueous matrix. GC-MS parameters are shown in the table below.

Table 4. Equipment, materials and parameters used for headspace analysis of samples and their corresponding conditions

Equipment	Operating Condition
Sample Injection Purge	Off 0.40 minuets, then On
Sample Volume	5 μL: Needle held in port for 0.08
Injection port	180°C
Oven temp	70°C, held constant
Mass Selective Detector	Single Ion Monitoring Mode, 95 amu
Carrier Gas	99.999% He, 0.949 mL/minute

The number of injections from individual calibration standards depended upon the reproducibility from injection to injection. Manual injection involves the human element. It is difficult to perfectly reproduce the injection volume, or to inject the sample at exactly the same rate every time. Consistency is the key, and the most difficult problem. Any and all variations in the sample introduction process can effect the concentration of analyte found in the sample. Based on the presence of procedural errors usually 2 to 3 or more injections were required to give peak areas within 10% of each other. Values judged as being outliers were discarded. Exactly the same procedure was conducted in the analysis of the samples. Since the variance of the sample peaks and calibration standard peaks were accepted within +/- 10%, any stated sample concentration could vary by at least +/- 10%.

The sample peak had a small but detectable amount of tailing. This certainly was another source of error, as some of the area of the tail was not used, or "cut-off" by the automatic integrator. Correspondingly, that amount of TCE was not found. This tailing was most likely due to an excessive interaction of the analyte with the stationary phase. The TCE has too high of an affinity for the dimethyl siloxane interior of the capillary column, and so adsorbs too strongly to it. This makes the band broader than desired and also results in some tailing. To cope with this problem, special columns are manufactured that limit this excessive interaction that is inherent with many halogenated solvents. A column with such a mobile phase was not used in this work, however. This GC-MS is intended for general use by the Chemistry Department, and so has a general purpose (dimethyl siloxane) column installed. Repeated changing of the column is not at all a practical alternative. The power and flexibility of the GC-MS

allowed this problem to be circumvented. By finding the predominantly occurring ion in the mass spectrum of TCE and selectively monitoring for this mass, only the signal due to ions of TCE at 95 atomic mass units was detected and quantified. This limited or nearly eliminated any interference from other species in the sample headspace.

3.2.4 BATCH SORPTION TESTING METHODOLOGY

Batch tests are used to find the sorption capacities of a given sorbent for a sorbate. The first test parameter determined is the time required for the establishment of distribution equilibrium at a specific concentration of sorbate for a specific mass of sorbent. Upon determination of an acceptable time to equilibrium, a sorption isotherm can be established. This is found by running batch tests with the same mass of sorbent across a wide range of sorbate concentrations. It determines how any amount of sorbent should perform in the presence of the sorbate under similar conditions.

All batch tests were run in the same manner. A cleaned BOD bottle was placed on the open top digital balance and tarred. A glass funnel was put in the mouth and around 5 grams of WRF-40 ground tire rubber was poured in and the funnel removed. The rubber weighed out to 1/100 of a gram precision. Any rubber that was stuck to the funnel was then not included in the test weight. Next, a solution spiked to the appropriate concentration of TCE was poured into the BOD bottle. Ground tire rubber is a very hydrophobic material and does not wet well. The bottle was shaken, mixed and struck on the table top to if not wet, then evenly distribute the ground rubber. It is a difficult material to work with. The bottle was filled until the rubber reached the bottom of the ground glass neck. At this point, TCE solution was slowly added and allowed to run down through the rubber. It was hoped that this would replace some of

the air pockets with contaminant solution. The glass stopper was put in the neck and waterproof tape was used to keep the integrity of the seal.

The only serious variations made to this methodology were changes in the concentration of TCE and the type of rubber used. Ground tire rubber is the principle thrust of this study, but for some tests, its use is impractical and would not yield any meaningful data. Chunk rubber was used in the 2 different batch tests; the cumulative desorption test and the repetitive sorb/desorb test. The rubber had to be removed from the batch reactor, blotted dry and put into a new batch reactor. This process would be impractical with ground rubber.

TCE is volatile and some amount was lost from the solution during it's pouring into the bottle and the process of sealing. To help to compensate for such procedural losses, a blank sample was included in each and every batch reaction. It was a BOD bottle with no rubber sorbent added. It was treated, processed and sampled in exactly the same manner as the bottles with sorbent. The blank's concentration was used later in the analysis step as the initial concentration (C_o) of TCE in the sample because it should have lost about as much TCE as did the samples.

The BOD batch reactors were placed in an end-over-end rotator for the duration of the test. Procedures for estimating adsorption of chemicals into soils, (in this case ground rubber), by Roy et al. (1991) were followed. The time required for equilibration was found by running identical batch reactors and their corresponding blanks for various time periods. Batch reactions were run at 75 ppm TCE for 72, 48, 24, 18, 6, and 3 hours at an ambient temperature of 21-23°C. According to EPA guidelines (Roy et

al., 1991), equilibrium is assumed when the amount of contaminant sorbed changes less than 5% between the timed batch reactions.

The changes in TCE concentration in the batch reactors containing ground rubber were compared with the sample blanks. These changes were considered only attributable to the adsorption of the contaminant into the rubber medium, as all other factors were held constant. All batches were sampled with a 30 mL class "A" volumetric pipette directly. The sample aliquot was then transferred into the 40-mL VOA vial and sealed with a screw cap and Teflon lined septum and stored in the dark at 7°C. All analyses were performed within 24 hours of sampling.

Once the time required for the system to equilibrate was found, batch tests were then used to determine the ability of ground rubber to sorb TCE over a range of concentrations. The process for the development of this isotherm is identical to that of finding the time for equilibration. The only difference is that the time of reaction is held constant and the concentration of TCE in solution is varied.

3.2.5 BATCH DESORPTION TESTING METHODOLOGY

The future intended use of this technology involves putting ground tire rubber in the contaminated ground water plume. It would be of great benefit if the sorbent could be regenerated in situ. Testing was conducted to determine how well the TCE could be desorbed from the rubber into water. Batch desorption tests consisted of placing a sorbent into a sorbate solution and allowing it to come to some equilibrium. The sorbent is then placed into a similar container with the same matrix, but this time without any of the sorbate present. The saturated sorbent is allowed to desorb for a certain amount of time. The freshly contaminated matrix is then sampled and the

sorbent is removed and transferred to a clean matrix again and the process repeated. The mass of the desorbed contaminant can be found by quantitative analysis of the desorption sample matrix and by knowing the volume of the desorption container.

Ground rubber would have been very difficult to work with in the desorption tests. The sorbent needs to be quantitatively removed from the batch reactor and all of the initial sample solution dried or rinsed off. Then it has to be quantitatively put into a batch reactor and filled with distilled water. This process would be haltingly difficult. Due to the errors in weights, drying and loss of sample to the atmosphere, no meaningful data would be found. Instead of ground rubber, whole chunk rubber was used. The rubber chunks were cut from a piece of what appeared to be semi tractor-trailer tire picked up along a local interstate. The rubber chunks were cut from the tread section of the tire and washed with only distilled water to remove any road soil.

The exact procedure consisted of first preparing two rubber samples. They were then put into 315 mL BOD bottles and taped shut. A blank was included to aid in the calculations of the amount of TCE sorbed. They were rotated in the batch reactor for three days. Being as these were individual whole chunks of rubber, it would take longer for the system to approach equilibrium. Three days seemed appropriate, although no studies were conducted to find equilibrium times for batch tests with whole chunk rubber. After the allotted time, aliquots of the solution were taken according to procedures previously outlined. The bottles were then drained and the rubber chunks quickly removed using forceps. The chunks were then patted dry with paper towels, but not rubbed at all to minimize the amount of paper material that could be carried into the next bottle. The rubber chunks were then put into clean BOD bottles filled with

distilled water and taped shut. They were then put into the rotator and allowed to desorb for three days. The process was repeated until a total of five iterations were performed. This technique was far from perfect because TCE is quite a volatile compound. The time taken to drain the bottles and then remove the rubber chunk, dry it and put it into the fresh bottle allowed a significant amount of the TCE to escape into the atmosphere.

3.2.6 PACKED BED COLUMN TESTING METHODOLOGY

Packed bed column tests are useful for determining the utilization efficiency of a known amount of sorbent under a given loading rate. Utilization efficiency measures the sorbent's ability to reach equilibrium with the sorbate, as determined from batch tests. The most common variables in this test are solution flow rate, sorbent mass and contaminant concentration. All of the column parts were cleaned and rinsed and the TCE contaminant solutions were prepared as previously specified.

The column was allowed to stand, clamped in position to dry. Some glass wool was packed into the open bottom of the column and then the threaded outlet and the glass frit were screwed on. The mass of ground rubber for the test was weighed. Using a powder funnel, the rubber was poured into the column. The column was tapped to help the rubber to settle. Previously, the rubber was more aggressively packed into the column with a wooden dowel, but this did not allow a high enough gravity flow of water. Glass wool was packed on top of the ground rubber bed and another glass frit dropped down on top of it. They would work together to keep nearly all of the rubber in the bed in place and prevent it from floating up the column. The frit was then tamped

down to better pack the ground rubber bed, but not compress it to the point that the flow of water is restricted below desired levels.

After filling and packing, the column was filled with distilled water. To get air out of the packed bed, the glass frit was pressed down with a wooden dowel repeatedly. Air pockets in the packed bed would cause short circuiting of some of the bed media, lowering the observed sorption capacity. However, due to the hydrophobic nature of ground rubber, it was not possible to remove all of the stray air pockets before the running of the test. The stopcock was opened and water was allowed to drain out as more distilled water was added at the head of the column. The slight downward currents would help pack the column uniformly. The column was drained until the level of the water was just above the top of the packed bed. Then the column was allowed to sit overnight to help ensure wetting of the rubber and to allow air pockets to escape without additional packing.

Immediately before running the column test, the TCE contaminant solution was prepared from the stock. The Teflon air sampling bag was filled with a long-stemmed funnel. This generated adequate head pressure to push the contaminant solution through the bag's valve. The valve on the bag was loosened by unscrewing it. A piece of Tygon tubing was used as the adapter between the funnel and the valve. It filled with surprising ease.

The settings on the pump to give a 5-6 mL/min flow rate had already been empirically determined and so set. The inlet to the pump was attached to the Teflon sampling bag and the system was purged of air. The empty head of the column was filled manually with contaminant solution. The inlet port was screwed onto the top of

the column and the tubing from the pump connected. The entire column was tipped to allow the air in the inlet region to be bled out of the inlet sampling port. When this was done, a septum was placed over the port, and the stopcock on the bottom was opened.

Sampling from the packed bed column test was done both of the influent and the effluent almost simultaneously. The samples were collected at predetermined volumes eluted during the test. The pump rate varied during the run, and so a 250 mL graduated cylinder was used to accurately measure the amount of solution passing through the bed. Effluent samples were collected by inserting a luer lock needle attached at the end of the column into the septum of the 5 mL vial. The cap of the vial was loosened to allow air to escape while keeping low the losses of TCE to the atmosphere. Influent samples were taken to account for any variation in the influent concentration of TCE caused by volatilization during preparation or transfer between containers and to account for any losses caused by sorption to surfaces before entering the packed bed column. Influent samples were collected by using the Kloehn 5 mL syringe to withdraw liquid through the septum port on the top of the column. The inlet sample was immediately injected into a 5 mL sample vial through the septum and sealed with as little air as possible. The samples were then kept at 7°C and analyzed within 24 hours.

The objective of these tests is to determine what volume of a specific contaminant concentration would be required to break though a given mass of sorbent in the column flowing at a certain rate. It would be best if the breakthrough value could be at the maximum drinking water concentrations of 5 ppb (EPA, 1994). However, this level is below that which could be detected with any certainty using the outlined

method. In this testing would be said to have occurred when the low baseline of background TCE signal began to rise significantly. The volume between the sample below and above the breakthrough region could then be used as the cut-off point in determining utilization efficiency of the sorption media. This was the used because the samples were taken as discrete aliquots of the effluent at specific points during the continually running test.

CHAPTER 4.

RESULTS & DISCUSSION

4.1 OUTLINE OF TESTS PERFORMED

The purpose of this research was to determine the ability of scrap tire rubber to act as a sorbent for TCE in an aqueous medium. The rubber used was both ground tire rubber and chunk rubber, depending upon the practicality of the use for the intended test. Whole chunk tire rubber was used in the repeated sorb/desorb testing and in the cumulative desorb testing. The batch tests to find the time for sorption equilibrium and the isotherm and the packed bed column test all used WRF-40 ground tire rubber. Previous to this research, the particle size distribution and the specific gravity of the ground tire rubber were found (Kershaw, 1996). The first tests helped to initially determine whether tire rubber would sorb TCE readily enough to justify further investigation. The isotherm tests were similar to the investigative equilibrium batch tests except they were used to find the capacity of ground tire rubber for sorbing TCE from an aqueous matrix.

Next, packed bed column tests were run to determine the utilization efficiency of the ground rubber. This would help to determine how practical the media would be to use in the field in remediation or containment applications. To supplement the use of ground rubber as a sorbent, cumulative desorption batch tests were run to learn how easily TCE could be desorbed from ground rubber into the atmosphere. Regeneration of the sorbent media is of interest because the installation and removal costs would far

out weight the price of the bulk sorbent material itself. Also, shipping and disposal costs of some sorbents can be so high that it makes them economically undesirable.

4.2 BATCH TESTS

4.2.1 EQUILIBRIUM DETERMINATION FOR TCE SORPTION BY GROUND TIRE RUBBER

To determine a sorption isotherm, one must first find the amount of time a certain mass of a specific sorbent must be in contact with a specific volume and concentration of that sorbate to reach equilibrium. The greater the amount sorbed in less time, the greater the affinity that sorbate has for the sorbent. The first test was run to determine the time required for running the tests for the isotherm.

Table 5. Time for Equilibrium

Bottle #	Equil. Conc.(ppm)	Rubber Mass (g)	Mass Sorbed (mg/g)	Time (hrs.)
162	10.5	5.00	2.164	72
270	10.0	5.00	2.195	72
173blank	45.4	0.00	-	72
139	14.9	5.00	2.920	24
168	10.5	5.00	3.193	24
53 blank	62.0	0.00	-	24
271	10.9	5.10	2.942	6
285	12.7	5.00	2.889	6
106blank	59.3	0.00	-	6
150	13.1	5.00	2.784	1
161	12.6	5.00	2.815	1
167blank	58.0	0.00	-	1

The table above contains some representative results from the batch tests used to determine the time required to establish a sorb/desorb equilibrium. The authoritative EPA resource document used for batch test procedures (Roy, et al., 1991) advises that equilibrium is approached at the minimum amount of time needed to establish a rate of change of solute concentration of less than 5% over a 24 hour

period. There was a great amount of variation in the "blank" samples in the early equilibrium batch tests. Most of this could be due to the poor sampling technique used for a volatile analyte. Many of the tests involved pouring the sample into a glass funnel lined with glass wool. The glass wool acted as a filter to separate the ground rubber from the aqueous matrix. This procedure exposed the sample directly to the atmosphere, allowing TCE to escape from the sample matrix.

The act of pouring the contaminant solution also acted to purge the volatile TCE from the sample. Also during filtration, bubbles were introduced into the long neck of the funnel. As sample flowed down, it pushed these bubbles out into the sample in the 40 mL vial and purged TCE from here as well. Efforts were made to limit both the time the sample was exposed to the atmosphere and the amount of bubbles introduced in the filling of the sample vial. The amount of bubbles introduced varied greatly, so this may be a source of major variation in the early tests.

Errors in the preparation of the experimental solutions and variations in losses of TCE made finding a change of less than 5% difficult. The initial concentrations of TCE differed somewhat due to the aforementioned losses from the contaminant solution matrix. A batch test that is run for 24 hours with a found blank concentration of 40 ppm would be difficult to compare to a similar sample run for 48 hours with a found blank concentration of 60 ppm. This would result in a change in the mass of TCE sorbed until equilibrium was approached. The best indication of equilibrium would be to calculate the mass of TCE sorbed per gram of ground rubber and look for a consistent change over time. Being as the mass of the ground rubber could be weighed much more precisely than the concentration of the TCE could be found, and

it would not change much throughout the tests (+/-0.1g), it could be considered constant. As long as the initial concentration of TCE used at the beginning of the test was constant within +/- 5 ppm, the sorbent capacity of the rubber for TCE should not change beyond the parameters of experimental precision. Then, the change found in TCE concentration from the blank sample to the sorbent sample could be used as the determining factor of time to equilibrium.

The "Mass Sorbed (mg/g)" column of Table 5 provides for the quickest way to analyze when the system reaches equilibrium. Multiplying the ppm sorbed by the rubber with the volume of the contaminant solution and then dividing by the mass of the ground rubber gives this value.

$$\frac{(58.0 - 13.1 ppm) \times 0.310 L}{5.00 g} = 2.784 mg/g \qquad (13)$$

The data indicates that this process is very fast. The mass of TCE sorbed in the batch reactors after 1 hour of exposure is essentially the same as that sorbed after 24 hours. The final TCE concentration dropped from around 60 ppm to 10-15 ppm, almost regardless of time. This suggests the establishment of equilibrium in very short time. However, it also indicates that not all of the TCE is or, at these levels, could be sorbed by the rubber. As was stated before, the sampling procedure evolved over time to some degree, and experience allowed for improved reproducibility, however aberrations could certainly occur. Based on the test results, a very conservative and practical value of 24 hours was chosen for the batch tests to come to equilibrium.

4.2.2 DEVELOPMENT OF AN ISOTHERM

Upon determining the time to equilibrium for the batch sorption process, an

isotherm can be found. An isotherm allows the prediction of the amount of contaminant that a particular mass of sorbent will be able to take up at a certain temperature and concentration of contaminant, allowing for equilibrium conditions. Five different concentrations of TCE solution were used. EPA outlined procedures call for changes in the soil:solute ratio to be made by changing the mass of the sorbent media. This method was modified so that the concentration of TCE was changed while the mass of the ground rubber and the volume of the contaminant solution were held constant. The ratios of 1:40, 1:60, 1:100 and 1:200 were used base on the EPA protocol. The 1:60 ratio was set as the 75 ppm TCE solution. The other concentrations that correlate to the above ratios were 30, 67, 125 and 250 ppm respectively. A 30 ppm solution was used instead of another prescribed ratio. This concentration was a better practical and experimental fit for the test. The milligrams of TCE sorbed per gram of ground rubber was calculated using Equation 8. The TCE isotherm data can be found in Appendix B.

Using the equilibrium concentration of TCE and the mg/g sorbed, the data was fit to the three isotherm models. The data was processed in accordance with the linearized models given in the EPA protocol (Roy, et al, 1992). This allowed the application of the linear least squares method to determine the goodness of fit. The direct plotting of the data points indicated that the linear model was the best fit. The Linear model r^2 value of 0.944 indicated a better correlation than the Freundlich model's r^2 value of 0.891. The equation of the best-fit line for the linear model is shown on the graph.

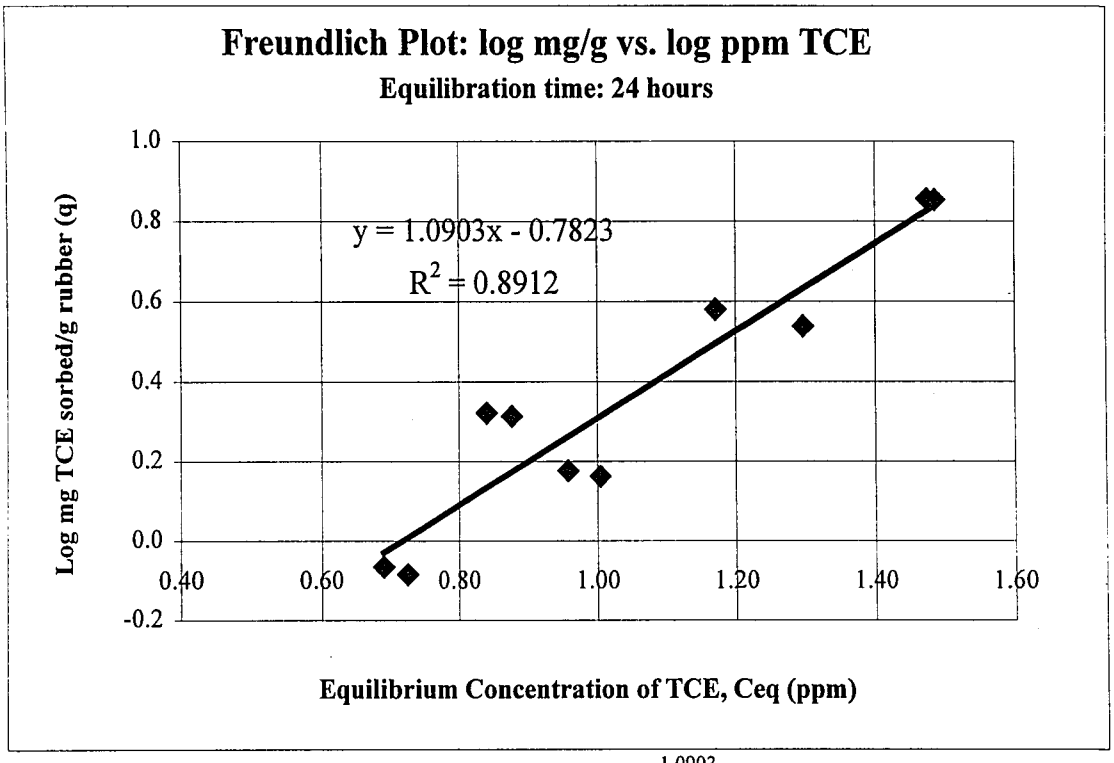

Figure 1. Freundlich isotherm plot: $q = (0.1651)\ C_{eq}^{1.0903}$

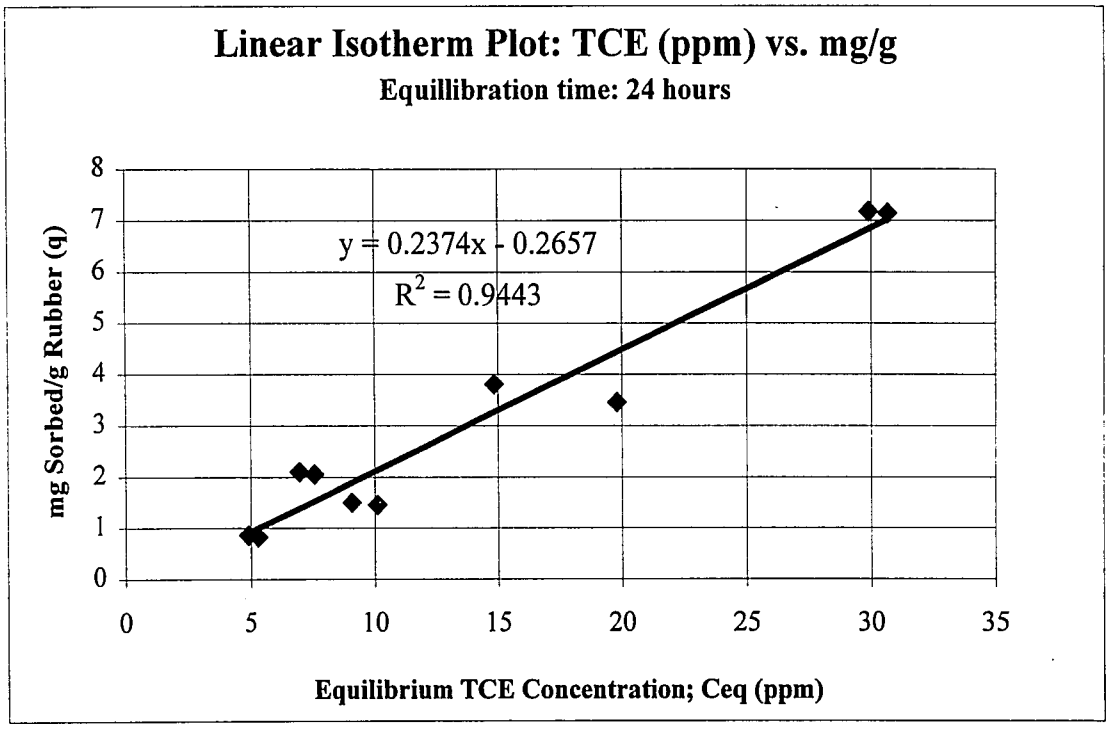

Figure 2. Linear isotherm plot: $q = 0.2374C_{eq} - 0.2657$

When the values for the Langmuir model were calculated, very little correlation was found with an r^2 of less than 0.3. If these tests were done over a much wider range of concentrations, a Freundlich model may have provided a better correlation. However, for the narrower range performed in this preliminary study, the linear model best represent the data.

The linear treatment of the isotherm data gives a line with an y-axis intercept of less than zero, (-0.2657). At an equilibrium concentration of 0 ppm TCE, there should not be any value for the sorbancy of the ground rubber. It should be near zero as well. A negative intercept, if interpreted directly, would suggest that TCE was desorbed from the ground tire rubber. This should not be the case, as the ground rubber was not previously exposed to TCE. A reasonable explanation for the negative intercept can be found by examining the lay of the data presented in Figure 1 and Figure 2. The value of –0.2656 is close to zero. Experimental error originating from the method could result in a scatter of the data that gives a y-intercept slightly above or below zero. From this series of data, a negative y-intercept is obtained. It is not beyond reason to interpret this low negative value as a value of zero.

A limitation of isotherms is revealed above. The isotherm cannot be extrapolated with any confidence above or below the experimental levels used in its development. Beyond this, it also will not provide a maximum capacity term. This is a useful number as it estimates the maximum amount of the contaminant species that is required to saturate the sorbent media.

4.2.3 ATTRIBUTABLE ERRORS IN BATCH TEST DATA

As stated previously, the GC-MS/headspace analysis technique was a combination of ASTM and EPA methods and the researcher's own experience in analyzing volatile samples. The ideal method would have been to collect, store and sample the aqueous aliquots with no headspace. A GC column with a stationary phase designed for halogenated solvents is available from major suppliers and would have given sharper peaks. These columns' stationary phase would withstand the direct aqueous injection of sample better than the stationary phase of the general purpose column used. Sharper peaks would allow for more accurate integration of the peak area, and little eluted sample would be missed. Direct aqueous injection would circumvent discrepancies in volumes of sample aliquots and headspace. It would not require time to for the equilibration of the TCE in the vapor phase and variations in room temperature at the time of the analysis. The most common routine method for analysis of volatiles is to use purge and trap to extract and preconcentrate the analytes (ASTM D 3871-84 EPA Method 5030 and 502.1). Purge and trap puts the analyte into an organic solvent, such as methanol at a much higher concentration than was originally in the sample. The matrix is then injected directly into the GC. For detection, an electron capture detector would have been ideal, although MSD has been shown to approach the ECD in sensitivity (Hewlett Packard, 1993). MSD's operate under low-pressure conditions, (10^{-4}-10^{-5} torr). As the sample elutes into the MSD, the pressure is pumped down. Sample is lost to the vacuum pump, and so only a small amount of the original sample's ions produce signal.

Most of the data was collected using a finalized version of the sampling technique. Pipetting the volatile sample does cause a loss of some of the TCE. Being

as all samples were treated the same, these losses should be fairly uniform. Losses of TCE during transfers should be similar between the blank and the two sample batch reactors. Pipetting served as a way of very accurately measuring the sample's volume as well as transferring it to the VOA vial. A few small bits of rubber from the batch reactors were unavoidably taken-up by the pipette. They would not cause much error because of their almost inconsequential mass and they were at equilibrium with the contaminant solution at the time of sampling. Using a syringe to measure and transfer sample would have greatly reduced the problem of uncontrolled headspace over the sample during measuring and transferal. However, the accuracy of the volume of sample that was added to the VOA vial would have been compromised. The samples were allowed to drain from the volumetric 30 mL pipettes. This was done into an open vial, but the tip of the pipette was kept under the surface of the solution in an attempt to minimize volatilization of TCE. This process took about 20 seconds and some loss of TCE certainly took place. Variations in the total volume of the VOA vial would change the amount of TCE vapor present in the headspace over the sample, considering that the liquid volume is constant at 30 mL. The VOA vials were not volumetric but their volumes varied by no more than 1.5 mL based on their weights when filled with water.

The filling of the batch reactors introduced error. The reactors were filled directly from the volumetric flask in which the contaminant solution was made. The act of pouring resulted in some of the TCE being purged from the aqueous matrix and into the atmosphere. As the contaminant solution is poured, the bubbles of air entering the volumetric flask and traveling through the solution purged some of the TCE. To

compensate for this, one reactor with ground rubber was filled, the blank was filled, and then the second reactor with ground rubber was filled. The blank reactor should then split the difference in losses between the two sample reactors. Ground rubber itself is not a well-behaved medium. Errors in rubber addition were minimized by using a funnel to add the sorbent. The funnel had already been "soiled" by the ground rubber so that tiny particles clinging to it would not be included in the final mass. The weight of the bottle was tarred-out and the weight of the soiled funnel was subtracted from the weight of the added rubber. Ground rubber wets very poorly. It often held air that, after rotation, became evident as air bubbles. These bubbles were not usually more than 5 mL. The blanks had bubbles that were around 1 mL. Some TCE would have been lost into these bubbles. This variation in bubble size loss would have been a source of error which could not be accounted for using the blank, albeit a small one.

Manual sample introduction of headspace gasses was most likely the largest source of error in the analysis. The samples were inverted the same amount of times and allowed to come to equilibrium. Sampling was then done with the 10 μL Hamilton Gastight syringe. Much of the precision of this method depended upon the analyst's ability to stop the syringe piston at the same point in the syringe barrel each time. This would translate into getting a consistent sample volume with each injection. The manual nature of this step introduced error. Sometimes as many as seven injections of headspace gasses from the same VOA vial were required to get consistent results. Clearly, this was the largest source of variation in the method. One problem, which was very difficult to detect, was the inadvertent pick-up of sample liquid stuck to the septum. The small punctures in the Teflon septum from previous

samplings allowed some sample to stick there by capillary forces. If the needle was then pushed though such a spot, then it could pick up some sample by capillary action as well. This small amount of liquid sample would then raise the apparent concentration of TCE in the sample significantly.

4.3 REPETITIVE SORPTION AND DESORPTION TESTS

The sorption/desorption tests are designed to investigate the potential of the ground rubber to desorb the contaminant load and to be regenerated by simply exposing it to the atmosphere. The first test was designed to show how readily TCE desorbed from scrap tire rubber into an aqueous matrix. The second test was designed to detect any significant changes in the ability of scrap tire rubber to sorb TCE after repeated sorb/desorb cycles. The cost of using ground tire rubber in a remediation scheme would be much less if it could simply be regenerated in situ with no loss of sorbent efficacy.

Both of the following tests were performed using individual pieces of whole chunk rubber. The two pieces used in the cumulative desorption test were different from the two pieces used in the repetitive sorb/desorb tests. Whole chunk rubber was required because of the handling of the sorbent material that was required. Ground rubber is far too difficult to handle to do any repetitive testing with it. The previous batch test's TCE solutions would need to be dried from the rubber before adding the rubber into the next batch reactor. Chunk rubber was needed for this.

4.3.1 CUMULATIVE DESORPTION FROM CHUNK RUBBER

If TCE comes to equilibrium between the rubber and the aqueous phase, then TCE absorbed within rubber should desorb into water that doesn't contain any TCE.

It would run down the concentration gradient and disperse into the water that does not contain TCE. If TCE is easily and quickly desorbed from tire rubber into an aqueous matrix, it's use as a protective barrier in spills may be compromised. If a spill occurred, the rubber would sorb the TCE, only to gradually desorb it into the groundwater. The more slowly the rubber desorbs the TCE, the more useful a barrier it becomes.

The procedure used for the cumulative desorption test is to use a whole piece of chunk rubber to sorb 75 ppm TCE solution in a batch reactor for three days. The cumulative amount of TCE sorbed was found by comparing the concentrations of TCE in the solutions from the blank and the two sample batch reactors. The chunks would then be transferred to reactors with only distilled water in them and allowed to desorb for three days. The water from the reactors was then sampled and analyzed. This test should normally be ended when concentrations approach the detection limit. This sorb/desorb test was stopped after nine days or three iterations. With the 2^{nd} and 3^{rd} samplings, there was no clear trend in the concentrations. The rubber chunks sorbed enough TCE to account for 310 mL of 46 to 47 ppm TCE solution. This is about 14 to 14.5 mg of TCE for each rubber chunk.

The tests were discontinued when the levels were found to be very low (2-3 ppm) and relatively constant. The concentrations appeared to be asymptotic and little further significant change was expected. Contamination and background were likely contributors to this low level signal. The total mass of TCE desorbed to the aqueous

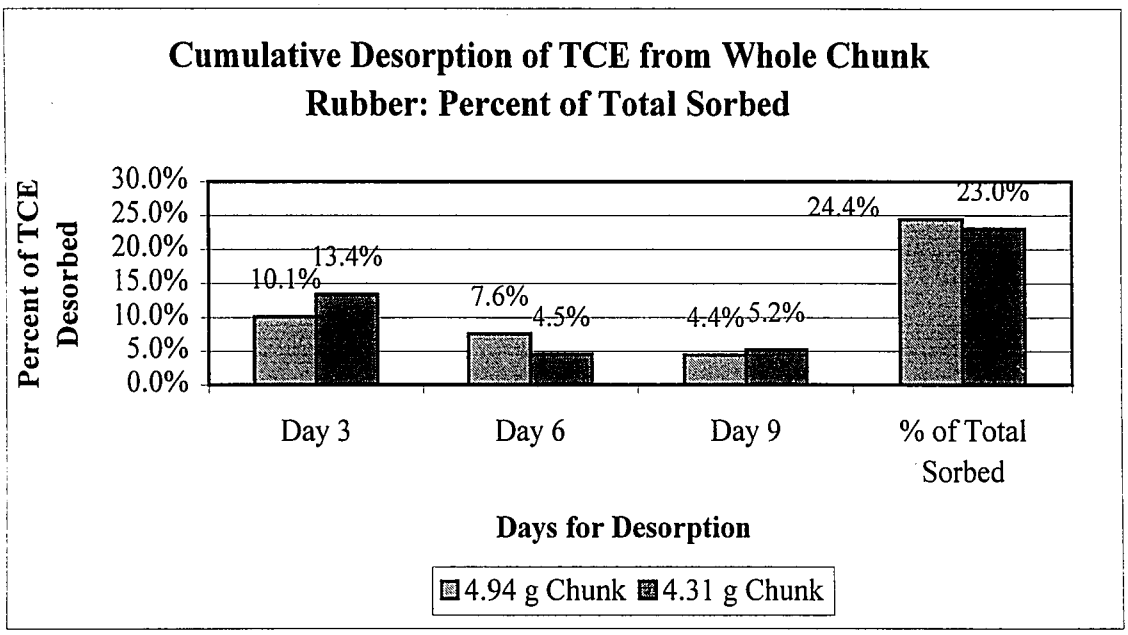

Figure 3. Cumulative Desorption of TCE in percent of total TCE initially sorbed.

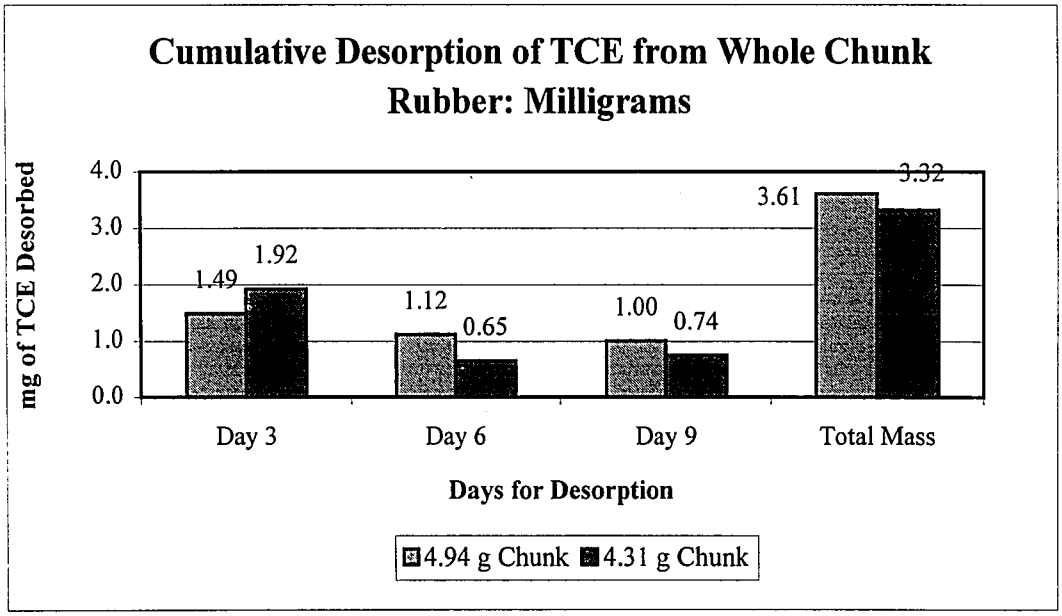

Figure 4. Cumulative desorption of TCE in ppm

phase was found to be 3.6 mg for the 4.94 mg chunk and 3.3 g for the 4.31 g chunk. This makes the cumulative desorption of the mass of TCE sorbed to be 25% for the 4.94 g chunk and 23% for the 4.31 g chunk.

A great deal of the TCE may have been lost to the atmosphere between the tests due to its volatility. The rubber chunks had to be retrieved from the batch reactors. The solution was first drained and then forceps were used to remove the rubber chunks from the neck of the reactor bottle. The chunks were then quickly patted dry with paper towels and put into the batch reactor bottles with distilled water. This period may have provided the opportunity for the TCE to escape the rubber chunk as vapor. Another reason for the low levels is that TCE maybe absorbed and retained by the ground tire rubber. The TCE absorbed within the chunk rubber matrix may have been very slowly coming to equilibrium with the aqueous phase.

Upon comparison of the blank and the two samples, the ability for chunk rubber to sorb TCE is seen by the drop in solution levels of around 47 ppm. At an equilibrium concentration of 21-22 ppm, the whole chunk rubber sorbs 3 to 3.3 mg/g of TCE. This value approaches the performance of WRF-40 rubber. This test did allow three days for the rubber to sorb the TCE and approach equilibrium as opposed to just one day for the ground rubber. No work was done to see just how quickly these large (nearly five gram) chunks of rubber would take to reach equilibrium. The greatest expense in the preparation of the raw materials for this remediation scheme is the grinding of the scrap tire rubber. It is a very tough material. If the rubber could be cut into small chunks and still closely approach the performance of ground rubber, then using it in passive remediation would be more desirable.

4.3.2 REPETITIVE SORPTION EFFICACY

The purpose of this test was to determine if the rubber was effected by repeated sorption and desorption of TCE. The test used the same batch type process

as was used with the cumulative desorption test. A blank batch reactor was included with each pair of sample batch reactors. Whole chunk rubber was used again because sorbent had to be removed, patted dry and then placed into another batch reactor. Ground rubber is not amenable to such handling. The two rubber chunks, of mass 5.49 g and 5.74 g were cut from the chunk of tire tread found along the local interstate. The rubber was exposed to a 75 ppm aqueous solution of TCE. Each batch reactor was rotated with the rubber chunk for one day (24 hours). More time could have been allowed for sorbing TCE, but approaching equilibrium was not necessary for the test. The repetitive sorb/desorb cycles would have effected the surface region of the chunk rubber. If there was any effect, it could be seen without establishing equilibrium. If there were a significant accumulation of TCE in the interior of the rubber chunk, then it would be detected by lower amounts of TCE taken up from the aqueous matrix. Much smaller ground rubber would desorb the TCE in less time.

After the completion of the reaction, a 30 mL sample was taken from the batch reactor. The rubber chunk was removed, patted dry and allowed to sit under the hood, exposed to the atmosphere, for 24 hours. The rubber chunk was then put back into a batch reactor filled with 75 ppm TCE solution and rotated for 24 hours. The process was repeated five times. Figure 5 below graphically displays the results of the test data. The results of the test indicate that there is only random, experimental change in the sorption capacity, (expressed as mg TCE sorbed per mg rubber). Due to the precision of the method, the observed range of values is not unexpected. The most important result of the test is that there is not a progressive decrease in the sorbancy of the rubber. The first two values are about the same as the last two values: 2.2mg/g.

Some of the errors could also have been caused by changes in temperature. However temperatures during the rotation of the batch reactor stayed within 4°C. A smaller chunk of rubber may have sorbed more TCE in the 24 hours due to its increased surface area to volume ratio. It also would have allowed the absorbed TCE to be lost more quickly for the same reason.

An encouraging prospect from the outcome of the repetitive sorb/desorb test is the ease with which the sorbent media is regenerated. There is no other process required other than exposing the sorbent to the atmosphere for an adequate amount of time. However, the TCE is then released into the atmosphere in the vapor phase. This release may have to be addressed in any future remediation scheme. The rapid and easy regeneration has more to do with the volatility of TCE. A less volatile contaminant would not desorb so quickly. Mild heating would be an effective aid in regeneration for slightly less volatile contaminants. This technique iscommonly used in solid phase extraction of a volatile component for G.C. analysis.

4.4 PACKED BED COLUMN TESTS

Batch tests are useful in gaining understanding about how the sorbent and sorbate behave together in a static situation. Nothing is added or removed while these tests are being run and, depending on the test requirements, the system approaches equilibrium. To emulate a more realistic situation, contaminant solution should flow through the sorbent media. A more accurate assessment can then be made about the sorbent's performance as a sorbent in a passive remediation scheme. A study of the application of a small scale column test to this end was done by John Crittenden at

Michigan Technological University (Crittenden et. al, 1991). An important value

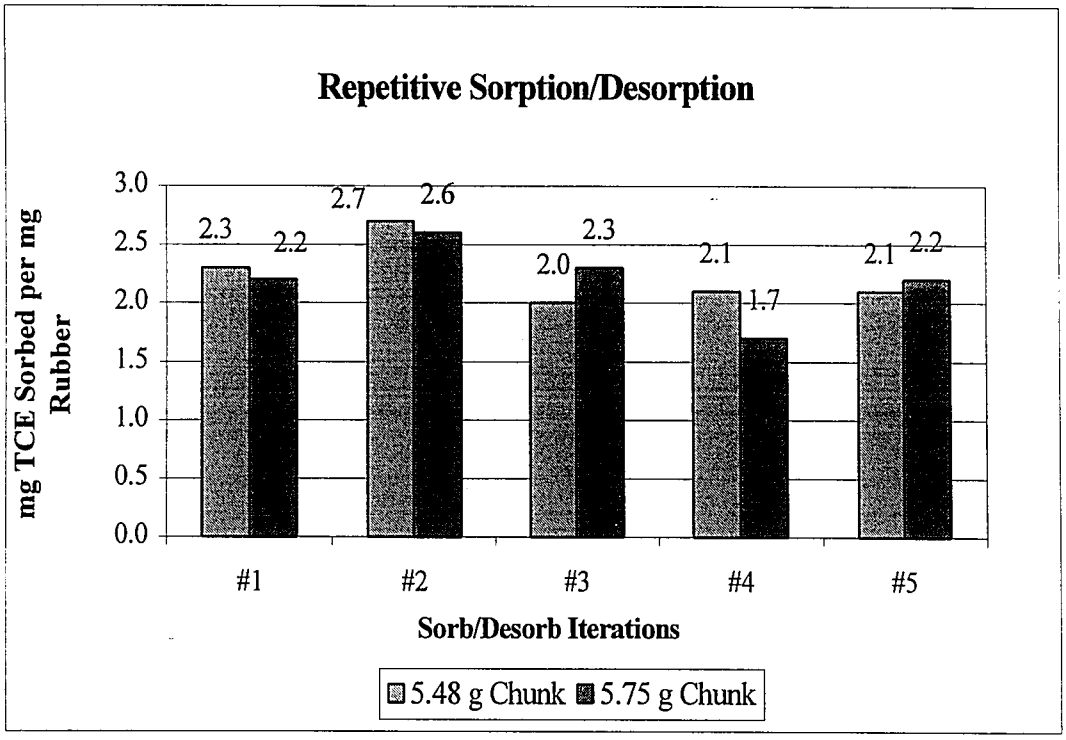

Figure 5. Repetitive sorption/desorption

found from a packed bed column test is the utilization efficiency, calculated by using Equation 8. This demonstrates whether the sorbent media retains a significant percentage of its performance found in the batch tests. This is a truer measure of the sorbent's performance in the field without undertaking a much larger and more expensive pilot run. Finding the sorbent media's utilization efficiency for certain contact times and contaminant concentrations would allow a sorbent media to be used most effectively in a remediation scheme.

As the TCE solution of a known concentration flows into and through the packed bed of sorbent, the TCE is kinetically sorbed and removed from the solution. The head of the packed bed contacts the highest concentrations of TCE. The ideal situation is that all of the sorbent media in the packed bed comes to equilibrium with

the sorption of the TCE greatly favored. Breakthrough would then occur only once all of the ground rubber had come to equilibrium with the TCE in solution. This would produce a sharp, steep breakthrough profile. Simply increasing or decreasing the flow rate of the contaminant solution can change the breakthrough profile.

The packed bed column test results are shown graphically by plotting the influent and effluent concentrations versus the number of empty bed volumes eluted at the time of sampling. One empty bed is the segment of the column or the cylindrical volume where the packed bed media is found. The diameter of the column and the length of the packed bed are used to find the empty bed volume. For this experiment, the height was 17.8 cm and the inner diameter of the column was 2.5 cm. This gives an empty bed volume of 87.4 cm^3. If 50 bed volumes were treated before breakthrough, and then the volume of treated solution would be 4.37 L. The volume treated per mass of sorbent is this value of 4.37 L divided by the mass of the ground rubber added to the column, 49.91 g.

The column used in such tests should have a diameter at least 50 times the mean diameter of the sorbent particles (Martin, 1978). A ratio less than this would allow for possible channeling in the sorbent media and short-circuiting of the contaminant solution. The column presently being used was 41.7 times the mean diameter of the ground rubber particles (Kershaw, 1996). This standard diameter column of 2.5 cm seemed adequate.

Figure 6 is a graphical representation of the column test data. It should be noted that the points on the graph indicate when samples were taken from the inlet port and from the outlet. The point indicating an effluent sample does not directly

correlate with treated influent sample. This type of control was not attempted. The influent was just sampled at the point in time that the indicated bed volumes were eluted. The influent was sampled to find the average concentration of TCE in the contaminant solution. A horizontal line was used to represent this value. Efforts were made to assure that the influent concentration of TCE would not change over the time of the test. Much of the variation in the detected level of TCE in the influent samples is assumed to be due to shortcomings in the sampling and analysis method. Sampling headspace gasses from the 5 mL VOA vials may have been the origin of the greater variation in this test's data. Such variation was not as commonly seen when the 40 mL VOA vials were used. Only 1.1 mL of headspace was used in this test. This was essentially sampling from the neck of the small vial. These small dimensions made handling the syringe more difficult. More headspace would have been desirable from a practical standpoint.

The linear representation of the TCE concentration in the effluent indicates a slight increase over the duration of the test. Some of this is due to the high effluent values at 16, 17.5 and 19 bed volumes. There was a sudden and inexplicable jump in the TCE concentration in this range. One explanation for this may be short circuiting. The aqueous matrix never fully wet the ground rubber, even though measures were taken to insure complete wetting. The column was filled with water and allowed to sit overnight and the ground rubber comprising the packed bed was compacted with a dowel repeatedly and allowed to sit overnight as well. As sample was being extracted through the inlet sampling port, a few large bubbles would occasionally escape from the packed bed. The negative pressure caused by the uptake of the syringe caused the

air pockets to expand and rise up through the packed bed. This air space was replaced by contaminant solution. This could have caused the solution just above the air pocket to jump down through the packed bed as it filled the space formerly held by the air pocket. The source of the initial readings of 6 ppm is not known. Contaminant solution had just started flowing through the packed bed column when the samples were collected. No TCE should have been present in the effluent at this point in the test.

The test was terminated before breakthrough was achieved. No sudden or significant increase in TCE was found in the effluent after treatment of over 2.4 L of solution (27.5 bed volumes). According to previous research done with benzene, given the conditions of the test, some initial breakthrough should have been detected (Kershaw, 1996). At room temperature, the solubility of benzene and TCE in water is 1,800 mg/L and 1,400 mg/L respectively (Montgomery, 1996). This would superficially indicate that, based on solubility alone, the TCE would break through before benzene would, given identical conditions. For this reason it seemed prudent to end the column test after 27.5 bed volumes. The results of the column test may be indicative of a stronger attraction of the TCE for the solid matrix of ground tire rubber than anticipated.

Finding the utilization efficiency from the test results brings up some interesting considerations. Initially, there should be no TCE present in the effluent when one bed volume is eluted. However, the first sample gave a value of 6.07 ppm. When finding the utilization efficiency, the milligrams of TCE sorbed per gram of ground rubber in the column is found with the breakthrough point representing the

total volume treated. This value is then divided by the mg/g sorption value of a batch test. The batch test that is used for comparison should have an initial concentration very close to that of the column inlet concentration of TCE. The found TCE concentration of the blank and that of the influent are much better indicators than the dilutions. It happens that an isotherm batch test had a blank final concentration of 75.5 ppm and the average influent concentration was 75.0 ppm. The background TCE signal prevented a small breakthrough from being detected. When compared with other column tests, a significant breakthrough concentration of TCE should have been easily seen. The only sudden surge in the concentration of TCE in the effluent then dropped back down to levels almost as low as those found at the outset of the test. The total number of empty bed volumes eluted was used because no clear breakthrough point was found. When Equation 8 is directly applied, the utilization efficiency is 99.5%. If the initial value of 6.07 ppm TCE is subtracted from the average found inlet concentration, the utilization efficiency is still 91.5%. This is very high when compared with an average value of 40% found in similar research involving BTEX contaminants (Kershaw, 1996). Breakthrough may have happened earlier, but the variation in the TCE values was too great to find a definitive point to indicate where breakthrough occurred, if at all. Breakthrough in fewer bed volumes would have decreased the numerator in the sorbancy equation and correspondingly lowered the utilization efficiency.

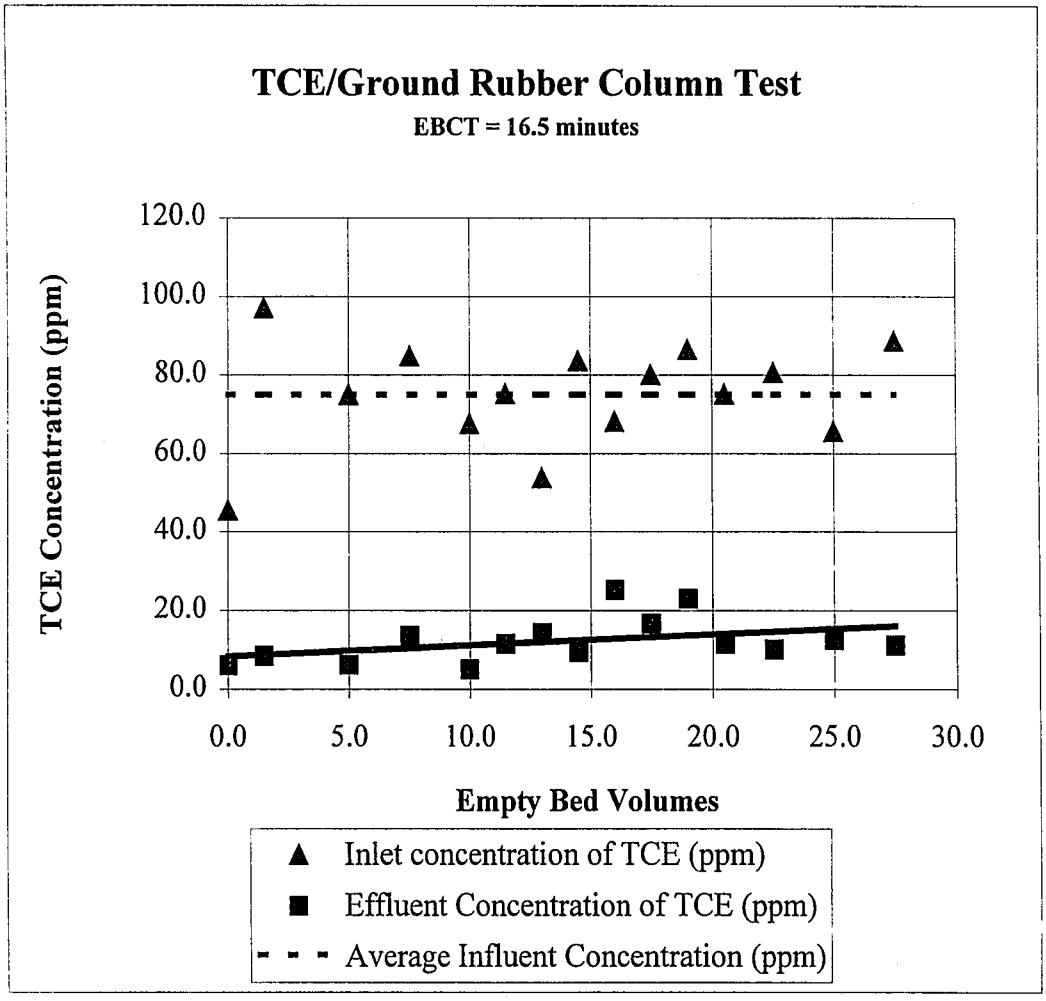

Figure 6. TCE column test data

Table 6. Useful column test values

Useful Column Test Values	
Mass of WRF-40 Rubber	49.92 g
Empty Bed Contact Time	16.5 minuets
Average Flow Rate	5.3 cm^3/minuet
Bed Volume	87.4 cm^3
Packed Bed Dimensions	17.8 cm long X 2.5 cm I.D.
Utilization Efficiency	91.5%

CHAPTER 5.

CONCLUSIONS AND RECOMMENDATIONS

5.1 BATCH TESTS

This research was conducted to determine the ability of ground scrap tire rubber to take-up trichloroethylene (TCE) from water. Preliminary batch tests were done to establish if ground rubber could sorb TCE from an aqueous matrix and to find the time required for the system to approach equilibrium. This information was used to help design experimental parameter for the development of a sorption isotherm for the system. The amount of TCE sorbed by the scrap tire rubber was determined by difference. A process blank containing no rubber was used with each test wherever applicable. The difference between the TCE concentration found in the blank batch reactor and the sample batch reactor was credited to sorption by the scrap rubber. Comparison of calibration standards and samples indicated an overall loss of around 40% of the initial calculated TCE present due largely to its volatility.

The results of the preliminary batch tests indicated that the sorption of TCE from water by the ground rubber was a fast process in the 75 ppm range examined. The batch tests did not require 24 a full hours in the rotator, but that amount of time was convenient and would assure that the system had closely approached equilibrium. The batch tests for the isotherms were run with constant volume and mass of rubber with a range of five TCE concentrations from 30 to 250 ppm. The actual, found TCE levels in the blank batch reactors ranged from 19 ppm to 143 ppm. The concentrations at equilibrium (C_{eq}) ranged from around 5 ppm to about 30 ppm and the sorbancy

magnitude ranged from about 0.85 mg/g up to 7.1 mg/g, respectively. The data was best modeled by the application of a linear model with the correlation coefficient being 0.9443. According to EPA values reported by Dobbs and Cohen, (1980), granular activated carbon (GAC) has a capacity to sorb 28 mg of TCE per gram at an equilibrium concentration of 1.0 mg/L. If the isotherm data is extrapolated below the experimental range, from roughly 5 ppm to 1 ppm, then application of the linear model dictates that the sorbancy value of roughly 0.85 should be reduced by one-fifth. This gives a value of 0.17 mg/g at 1.0 mg/L TCE concentration which is 0.6% of the GAC value.

To minimize the cost of using ground tire rubber and increase interest in its use as a passive remediation sorbent, regeneration is proposed. Due to practical limitations and handling difficulty, whole chunk rubber was substituted for ground tire rubber in these tests. The experiments used the same batch reaction procedures as were used to develop the isotherm. The chunk rubber was allowed to sorb in a 75 ppm TCE solution for one day and then removed and placed under the hood for one day to allow the volatile TCE to desorb to the atmosphere. No significant changes in the ability of the rubber chunk to sorb TCE was found after five iterations of the test. Therefor, it can be concluded that tire rubber can be regenerated as a sorbent when exposed to air and the contaminant is allowed to volatilize.

A cumulative desorption test was run to study how TCE would be desorbed back into an uncontaminated aqueous matrix. Chunk rubber was again used due practical handling limitations. The chunks were allowed to sorb TCE in a 75 ppm solution for three days. The chunk was then removed, blotted dry and then placed into a batch reactor filled with distilled water. The amount of TCE desorbed into the water

was low and did not show a predicted continual decrease with repeated new desorption batch tests. The tests were terminated when the amount of TCE desorbed appeared to become asymptotic. About 22% of the sorbed TCE was cumulatively desorbed into the uncontaminated aqueous matrix.

5.2 COLUMN TEST AND UTILIZATION EFFICIENCY

Packed bed column tests are the next step to evaluate the potential of the ground rubber for field use as a passive remediation sorbent. This helps to determine how much ground rubber will be needed given the levels of contamination and the flow rate of the ground water. The utilization efficiency is that percentage of the ground rubber's sorbant ability that is retained in the column test relative to the batch test values. Control of experimental parameters such as the empty bed contact time (EBCT) and concentration will determine the value of the utilization efficiency. The utilization efficiency was found to be 95.1% with an EBCT of 16.5 minuets and an average inlet concentration of 75.0 ppm. The breakthrough point, which determines the treated volume and so effects the utilization efficiency, was not clearly detected in these tests. In conclusion, these preliminary studies show that ground tire rubber has the potential to be used effectively as a sorbent in passive remediation where TCE is present.

5.3 RECOMMENDATIONS FOR FUTURE RESEARCH

There was no clear evidence of a breakthrough point for the column test. This test should be performed again, with many more bed volumes being used before the test is completed. The amount of TCE should not be significant in the earliest bed volumes

collected. The source of the observed TCE contamination at the beginning of the column test was not found in the course of this research.

All of the work in this research was done with DI water. Groundwater contains many organic and inorganic components that may or may not interfere with the ground rubber's ability to sorb TCE. Other hydrophobic substances are present in ground water. These may compete with the TCE for sorption or make the aqueous matrix more hospitable to such hydrophobic species. This would reduce the entropic driving force for TCE to leave the aqueous phase.

The method used for analysis was not one of high precision. Much lower levels of TCE are present in groundwater. The EPA limit for TCE for community drinking water systems is 5 parts per billion. It would be advantageous to be able to reliably measure TCE in groundwater at these levels. Instrumentation specifically for the analysis of environmental samples would make the method more precise and accurate. A G.C with a column designed for separation of halogenated solvents and an ECD detector is needed. If headspace analysis is to be done, the samples should be heated to cause more TCE to go into the vapor phase. This would effectively raise the amount of TCE to be detected. Another method like purge and trap would allow much lower levels of TCE to be detected.

In final preparation for a pilot scale test, other solvents which are commonly found with TCE should be assessed as to how well they are sorbed by ground tire rubber. TCE is of primary concern, but other chlorinated organic solvents are usually found in the groundwater with TCE. The cost vs. benefit of using ground tire rubber in exception to other sorption media like granular activated charcoal need to be further

explored. A pilot scale test would allow the cost of such a remediation scheme to be assessed. Also, an *in situ* regeneration scheme should be explored. The cost of recovering the ground tire rubber may prove prohibitive if it must be excavated for regeneration. The benefits of reuse of this scrap tire rubber "resource" should be considered as well. Grinding or chunking of scrap tire rubber helps it to be landfilled more effectively. However, beyond this benefit, it doesn't have any other positive returns. Scrap tire rubber could be ground, used for the removal of NAPLs from an aquifer and then landfilled. In this case, the expensive process of grinding tire rubber to a fine consistency would be offset to some extent by its use as a permeable barrier medium in a passive remediation scheme. If the scrap tires could be chunked or shaved instead of ground, such use would be even more advantageous. Grinding this tough material is a much more intensive process than chunking it and accounts for most of its cost as a raw material. Future research may suffer from variations in the scrap tire rubber's chemical composition. Rubber formulation change between manufacturers and series of tires. If ground tire rubber were made from a large sampling of tires, then these differences in elastomer composition could be made less significant. In this study, it was shown that the performance of the whole chunk rubber approached that of ground tire rubber for the sorption of TCE.

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APPENDIX A.

ESTABLISHMENT OF SORPTION EQUILIBRIUM

Appendix Table 1. TCE sorption data for the establishment of time for equilibrium

Bottle #	Found Conc. (ppm)	Rubber Mass (grams)	TCE Sorbed (ppm)	Mass Sorbed (mg/g)	Time (hours)
162	10.5	5.00	34.9	2.164	72
270	10.0	5.00	35.4	2.195	72
173 Blank	45.4	0.00	-	-	72
109	7.6	5.00	11.5	0.710	48
284	6.7	5.00	12.3	0.761	48
28 Blank	19.0	0.00	-	-	48
139	14.9	5.00	47.1	2.920	24
168	10.5	5.00	51.5	3.193	24
53 Blank	62.0	0.00	-	-	24
52	13.2	5.00	67.1	4.160	18
161	12.4	5.00	67.9	4.210	18
176 Blank	80.3	0.00	-	-	18
271	10.9	5.10	48.4	2.942	6
285	12.7	5.00	46.6	2.889	6
106 Blank	59.3	0.00	-	-	6
29	12.6	5.00	39.0	2.418	3
160	11.5	5.00	40.1	2.486	3
109 Blank	51.6	0.00	-	-	3
150	13.1	5.00	44.9	2.784	1
161	12.6	5.00	45.4	2.815	1
167 Blank	58.0	0.00	-	-	1

APPENDIX B.

TCE/GROUND RUBBER ISOTHERM DATA

Appendix Table 2. Isotherm data

Calculted Conc. (ppm)	Bottle #	Rubber wt. (grams)	Found Conc. (ppm)	Ave. Conc. (ppm)	Ave. Bottle Volume (mL)	TCE Sorbed (ppm)	Density Ground Rubber (g/mL)	Sorbancy mg/g
30	167	5.01	5.5, 5.0, 4.2	4.90	315	13.70	1.20	0.861
30	284	5.08	5.6, 5.0	5.30	315	13.30	1.20	0.824
30	162	0.00	19.2, 18.0	18.60	315	-	-	-
67	28	5.01	10.0, 10.2	10.10	315	23.10	1.20	1.45
67	160	5.06	9.8, 8.9, 8.5	9.07	315	24.13	1.20	1.50
67	150	0.00	33.9, 32.5	33.20	315	-	-	-
75	158	5.02	7.1, 7.8, 7.7, 7.5	7.53	315	32.81	1.20	2.06
75	273	5.01	7.2, 7.0, 7.0, 6.5	69.3	315	33.41	1.20	2.10
75	109	0.00	39.4, 39.3	40.33	315	-	-	-
125	106	5.08	20.9, 17.8, 20.7	19.80	315	55.70	1.20	3.45
125	132	5.02	14.6, 15.1	14.85	315	60.95	1.20	3.80
125	109	0.00	73.6, 74.8, 78.1	75.50	315	-	-	-
250	168	5.05	29.4, 31.0, 31.6	30.67	315	114.53	1.20	7.14
250	270	5.06	30.5, 29.3	29.90	315	115.30	1.20	7.17
250	271	0.00	142.6, 147.8	145.20	315	-	-	-

APPENDIX C.

DATA FOR THE FREUNDLICH AND LANGMUIR ISOTHERM PLOTS

Appendix Table 3. Freundlich and Langmuir plot data

Equilibrium TCE Concentration (ppm)	Sorbancy (mg/g)	log(Equil. Conc)	Log of Sorbancy	Langmuir y-axis	Langmuir x-axis
4.90	0.861	0.690	-0.065	5.69	4.90
5.30	0.824	0.724	-0.084	6.43	5.30
10.10	1.45	1.000	0.162	6.96	10.10
9.07	1.50	0.958	0.176	6.04	9.07
7.53	2.06	0.877	0.313	3.66	7.53
6.93	2.10	0.841	0.322	3.30	6.93
19.80	3.45	1.297	0.537	5.74	19.80
14.85	3.80	1.172	0.580	3.90	14.85
30.67	7.14	1.487	0.854	4.30	30.67
29.90	7.17	1.476	0.856	4.17	29.90

APPENDIX D.

CUMULATIVE DESORPTION DATA

Appendix Table 4. Data from the Cumulative Desorption test

Sorb Date	Sorb Rubber (grams)	Sorb Average ppm	Sorb Change in ppm	Sorb Weights (mg)	Sorb % Desorbed of Total
9/30/97	0.00	68.3			
9/30/97	4.94	20.8	47.5 ppm	14.73 mg TCE	
9/30/97	4.31	21.9	46.4 ppm	14.38 mg TCE	
Desorb	Desorb	Desorb	Desorb	Desorb	Desorb
10/03/97	4.94	4.8		1.49	10.1%
10/03/97	4.31	6.2		1.92	13.4%
10/06/97	4.94	3.6		1.12	7.6%
10/06/97	4.31	2.1		0.65	4.5%
10/09/97	4.94	3.2		1.00	4.4%
10/09/97	4.31	2.4		0.744	5.2%
	Total Desorbed:			Total % Desorbed:	
	4.94 g chunk =	11.6 mg		4.94 g chunk =	24.4%
	4.31 g chunk =	10.7 mg		4.31 g chunk =	23.0%

APPENDIX E.

REPETITIVE SORB/DESORB TEST DATA

Appendix Table 5. Data from the Repetitive Sorb/Desorb test

Iteration	Bottle Number	Rubber (grams)	Average Conc. (ppm)	Sorbancy (mg/g)	Percent of Blank
1	271	0.00	58.4	-	
1	106	5.49	17.3	2.3	29.6%
1	168	5.75	16.9	2.2	29.0%
2	284	0.00	64.8	-	
2	132	5.48	15.7	2.7	24.2%
2	161	5.74	17.0	2.6	26.2%
3	158	0.00	67.7	-	
3	52	5.48	30.3	2.0	44.8%
3	150	5.74	26.9	2.3	39.7%
4	167	0.00	51.9	-	
4	28	5.49	15.0	2.1	29.0%
4	109	5.75	21.0	1.7	40.6%
5	273	0.00	62.4	-	
5	106	5.48	25.6	2.1	41.0%
5	271	5.75	21.9	2.2	35.1%

APPENDIX F.

TCE/GROUND RUBBER PACKED BED COLUMN TEST DATA

Appendix Table 6. Data from the Packed Bed Column Test.

Vial #	Bed Volumes (87.4 mL/b.v.)	Inlet Conc. (ppm)	Outlet conc. (ppm)	Flow Rate (mL/min.)
1	0.0	45.4	6.07	6.0
2	1.5	97.0	8.46	3.5
3	5.0	74.8	6.28	5.0
4	7.5	84.7	13.5	6.0
5	10.0	67.5	5.04	5.5
6	11.5	75.1	11.5	5.3
7	13.0	5.37	14.2	5.5
8	14.5	83.4	9.45	5.4
9	16.0	68.0	25.12	6.0
10	17.5	79.9	16.6	5.5
11	19.0	86.3	22.9	4.2
12	20.5	75.0	11.6	5.3
13	22.5	80.5	10.1	4.7
14	25.0	65.5	12.5	6.1
15	27.5	88.5	11.2	5.7
Ave.		75.0		5.3

VITA:

Jason P. Beary was born on December 29, 1969 in the small industrial town of Oil City, Pennsylvania to Gerald and JoAnne Beary. In June of 1988, he graduated from Cranberry Area High School and decided that chemistry would be his choice of professions. In May of 1992, he earned a Bachelor's of Science in Chemistry from Gannon University in Erie, Pennsylvania. He then spent the following summer at the University of California, Riverside working with cholecalciferol in the research group of Professor Bill Okamura. The following three years were spent living near Washington D.C. in the suburban community of Fairfax Station, Virginia. Jason worked for companies that were involved in environmental remediation and analyzed soil and water samples. In a one and one-half year term at CHEMetrics, a water analytical test kit manufacturer, he developed a new test using Chlorophosphonazo III to visually determine the hardness of water down to 100 ppb. Disappointed with the job prospects in the Washington, D.C. area, and determined to return to a more bucolic setting in Pennsylvania, he matriculated to Lehigh University in Bethlehem to pursue an advanced degree in chemistry. To allow the maximum benefit from his years in the environmental industry, he chose to do research for Dr. Sibel Pamukcu in the Civil & Environmental Engineering Department. Jason intends to stay in Pennsylvania and use his education and experience to help save, preserve and restore the woods and streams of the Keystone State that have been so important to him throughout his life.

END OF TITLE